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FINAL REPORT
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FINAL REPORT

DISPOSAL OF CHEMICAL WASTES

ROCKY MOUNTAIN ARSENAL

[REDACTED]

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DEPARTMENT OF THE ARMY

[REDACTED]

CORPS OF ENGINEERS

OMAHA DISTRICT

CONTRACT NO. DA-25-066-eng-3452

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Rocky Mountain Arsenal
Information Center
Commerce City, Colorado

The Ralph M. Parsons Company
617 South Olive Street
Los Angeles, California

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FOREWORD

During the summer of 1954 several farmers, located adjacent to the northwest boundary of the Rocky Mountain Arsenal, reported that serious injury was done to their crops when well water was used for irrigation. There was a strong feeling among these farmers and others who were concerned with the problem that the injury was caused by some toxic substance in the underground waters, and that this toxic substance came from the Arsenal. The United States Army Corps of Engineers negotiated a contract with The Ralph M. Parsons Company to determine the most economical measures that could be taken to reduce the possibility of contamination of underground waters by the various industrial wastes from the chemical operations at the Arsenal. A secondary phase of the contract was to attempt to determine if there were a toxic component in the water that could cause the crop damage and, if possible, recommend corrective measures to eliminate this toxicity.

This report includes a study of the disposal of the chemical by-products and wastes from all of the chemical operations presently being carried out or contemplated at the Rocky Mountain Arsenal. There is also an evaluation of all reasonable processes for converting these by-products to saleable materials and a survey of the potential markets for such materials.

Qualified consultants were called in to assist in the study of the problem of crop damage and various waters were analyzed in an attempt to identify the toxic constituents of these waters. Their conclusions and recommendations will be presented and analyzed in a supplemental report to be issued later.

The purpose of this report is to present the findings resulting from a study of the problem, to analyze the possible remedies, and to make recommendations as to the most economical means for reducing or eliminating the problem.

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1113-AC6	Process Flow Diagram Chloride Recovery System for Plant No. 2
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SUMMARY

1. An extensive study has been made of the problem of disposal of chemical wastes from the various chemical plant operations at the Rocky Mountain Arsenal. A market survey indicates that a market exists for some of the pure hydrochloric acid and all of the chlorine which could be produced at the Arsenal. A material balance prepared for Plant No. 1 showed that 6 to 8 per cent of its product is being lost in its by-product stream. Not only is it worthwhile to recover this valuable material but the by-product acid must be purified of this contamination before it is sold or used.
2. A study of the disposal of these wastes by all possible methods which would avoid the risk of contamination of underground fresh water supplies indicated that the following series of measures offered the most practical and economical scheme:
 - a. Immediately reduce to a practical minimum the volume of contaminated water discharged from all plants.
 - b. Immediately install an asphalt membrane seal in the existing 142 acres of reservoirs for an estimated cost of \$667,000, and use for temporary disposal of plant wastes. Plant No. 1 can be operated at about twenty — 3 per cent of capacity with this disposal facility.
 - c. Design and construct an acid purification plant for the by-products from Plant No. 1 for an estimated cost of \$2,050,000. Initiate a laboratory program for an estimated cost of \$5,000 to develop plant design data.
 - d. Design and construct facilities for neutralizing of surplus acid and for transferring resulting brine to existing evaporator plant, crystallizing and stockpiling salt. These facilities are estimated to cost \$144,500.
 - e. Produce and sell as much pure acid as can be absorbed by the existing market. Neutralize any surplus acid and stockpile resulting salt.
 - f. Develop a process in the laboratory to purify the chlorides produced from Plant No. 2. This laboratory program can be initiated for four to five thousand dollars.

- g. Dump all miscellaneous other wastes from the plants to the sealed reservoir system for solar evaporation.

This disposal scheme will require an estimated total investment as summarized below:

Sealing Reservoirs	\$ 667,000
Purification Plant	2,050,000
Laboratory Programs (2)	10,000
Salt Stockpiling Facilities	<u>144,500</u>
TOTAL PROJECT COST	\$2,871,500

It is estimated that this system will result in a reduced operating cost for disposal of the chlorides from Plant No. 1 below the cost of the present method and in addition will recover eight to nine thousand pounds of Plant No. 1 product per full operating day, which is now being lost using the present operating facilities and methods.

3. Further investigation of the Grosvenor-Dow process for the catalytic conversion of hydrogen chloride to chlorine (as developed by Hercules Powder Company) is strongly recommended. On the basis of the data presently available, this process offers the most dependable and economical scheme for disposal of the chlorides from Plant No. 1. Hercules Powder Company estimates that such a plant would require an investment of \$1,350,000.
4. Conversion of the pure hydrogen chloride to chlorine via salt electrolysis in the existing plant is estimated to increase the cost of chloride disposal from Plant No. 1 over present or other proposed methods. We expect that conversion of the crude acid to chlorine by this method would be inoperable or considerably more costly than conversion of the pure acid. A comparison of the investment and operating costs of these various disposal schemes are given in Table I.
5. With all of the plants in full production disposal of the chemical wastes to sealed reservoirs or injection wells would be prohibitively costly both in investment and in operation. These costs would be further increased if the by-products from Plant No. 1 were dilute, as is necessary if not purified of contamination with phosphorus and fluorine compounds. ✓

TABLE I

SUMMARY OF ESTIMATED COSTS OF
DISPOSAL OF CHEMICAL WASTES

Basis: Plants in full production. Costs of rehabilitating existing facilities not included. All methods, except "A", expected to recover 8 to 10,000 pounds daily of Plant No. 1 product.

<u>Disposal Scheme</u>	<u>Investment</u> \$	<u>Operation</u> \$/month
Method A - Present Scheme Neutralize and dump to existing lakes;	Not estimated but probably very small	63,591
Method B - Electrolysis to Chlorine; Acid Purification Plant \$2,050,000 Brine Transfer System 30,000 Sealed Reservoirs 667,000	2,747,000	90,497
Costs of electrolysis of impure brine not estimated because expected to be inoperable and would not recover lost product.		
Method C - Stockpiling Pure Salt; Acid Purification Plant \$2,050,000 Brine Transfer and Solids Handling 144,500 Additional Storage 195,400 Sealed Reservoirs 667,000	3,056,900	95,238
Method D - Catalytic conversion of HCl to Chlorine; Acid Purification Plant \$2,050,000 Catalytic Chlorine Plant (estimate by Hercules) 1,350,000 Sealed Reservoirs 667,000	4,067,000	10-30,000
Method E - Sale of some pure HCl, stockpile surplus as salt; Acid Purification Plant \$2,050,000 Brine Transfer and Solids Handling 144,500 Sealed Reservoirs 667,000	2,861,500	51,695

TABLE I (Cont'd)

Others: The cost of disposal of the entire waste streams to sealed reservoirs without recovery of Plant No. 1 product was not estimated because of the excessive volume to be handled (500 to 600 gpm) and the loss of valuable material.

CHEMICAL WASTE PROBLEM

STREAM SOURCES AND VOLUMES

The chemical wastes from the various plant operations are presently being discharged as water solutions to a series of contaminated lakes. A certain amount of water evaporation from these lakes takes place, but the total volume of the discharges is presently so large that only a portion of the water is eliminated in this way. The level of these contaminated lakes remain essentially static because of seepage of the waste water into the ground.

As most of the chemical wastes are water-soluble salts, the large volume of water in which these salts are dissolved creates a very difficult disposal problem. Solar or steam evaporation of these dilute solutions would be prohibitively costly.

Measurement of the volume of water discharged by the various chemical plants into the lake system is relatively crude but the total instantaneous maximum quantity is approximately 1,000 gallons a minute. The average input to the lakes amounts to about 570 gallons a minute.

Investigation of the process water systems of the various plants revealed the sources of the various streams going into the lake:

In the Chemical Corps Plant No. 1, an instantaneous use of 850 gpm was measured during a peak operating period in June 1955. Although there was no means for measuring the individual water usages in the plant, it is estimated that 400 to 600 gpm were used in barometric condensers on steam jets, about 100 gpm in the gas scrubbers, and the rest in equipment and floor washdown.

The brines discharged from the Plant No. 1 scrubbers must be kept dilute to avoid plugging in the scrubbers. If the present off-gas composition continues, the highest average dissolved solids content that could be maintained in this brine is about 5 per cent by weight. Disposal of 2,800 tons of solids a month, as could be expected in future operations would require a discharge of 13 million gallons of water a month or about 300 gpm from the scrubbers alone.

The Shell Chemical Corporation are presently dumping about 100 gpm of effluent into the contaminated lake. This effluent volume was recently reduced from 185 gpm when Shell's plant producing hexachlorocyclopentadiene, "Hex", was shut down and put in standby. A large portion of Shell's present effluent is cooling water

from shell-and-tube condensers. This cooling water is not presently circulated into the normal Derby Lake cooling system as there is a possibility of leakage in the condensers which would permit Shell's product to get into Derby Lake. Shell's products are quite toxic to wildlife. Monitoring devices to detect such a contamination of the water stream are not considered to be dependable.

DISSOLVED MATERIALS

In the production of the various desired materials from the chemical plants at the Rocky Mountain Arsenal, undesirable by-products are also made and must be disposed of.

The principle by-product from the various operations is anhydrous hydrogen chloride gas contaminated with other constituents. The present plant practice is to neutralize this acid with an excess of caustic soda and dump the resulting alkaline brine to the primary contaminated lake. As these salts are water soluble, they are being carried into the underground strata by the water seeping from the lakes.

The significant quantities of salts that are being dumped into the lake at present and the expected future quantities to be disposed of are given in Table II .

TABLE II

QUANTITY OF SOLIDS TO BE DISCARDED

TONS/MONTH

PRESENT	Chem. Corps Plant No. 1	Chem. Corps Plant No. 2	Shell Chem. Corp.	Total
Sodium Chloride, NaCl	400	None	None	400
Sodium Fluoride, NaF	40	None	None	40
Sodium Hydroxide, NaOH(100%)	140 *	None	None	140
Sodium Methyl Phosphonate $\text{CH}_3\text{PO}(\text{ONa})_2$	110	None	None	110
Sodium Acetate and Sulfate	<u>None</u>	<u>None</u>	<u>130</u>	<u>130</u>
Total	690	None	130	820
<u>FUTURE EXPECTED</u>				
Sodium Chloride, NaCl	1,630	1,349	None	2,979
Sodium Fluoride, NaF	163	None	None	163
Sodium Hydroxide, NaOH	570 *	None	None	570
Sodium Methyl Phosphonate	475	125	None	600
Sodium Acetate and Sulfate	None	None	130	130
Aluminum Hydroxide	<u>None</u>	<u>391</u>	<u>None</u>	<u>391</u>
Total	2,838	1,865	130	4,833

* This quantity of free caustic dumped to the lake results from the present practice of using 140 per cent of the theoretical requirements. This excess quantity can and does fluctuate according to variations in operational procedures.

MARKET SURVEY

An extensive market survey was made covering all of the major chemical companies concerned with manufacture and sale of chlorine or chlorides in any form.

SODIUM CHLORIDE, NaCl

The following companies showed interest in purchasing sodium chloride:

1. Morton Salt Company, Chicago, Illinois
Offered \$8.00 a ton for 8 to 10 tons a day of "food grade" salt.
2. Carey Salt Company, Wichita, Kansas
Offered \$4.50-5.00 a ton for 15 tons a day of "food grade" salt. Specified crystal sizes difficult to attain in existing equipment.

HYDROCHLORIC ACID, HCl

The following companies showed interest in the production of hydrochloric acid at the Arsenal:

1. Frontier Chemical Company, Wichita, Kansas
Offered \$8.00 a ton, f.o.b. Denver in Frontier's railroad cars, for 50 tons a day of 20° Baume HCl, "food grade".
Offered \$5.00 a ton, same freight terms and quantity, for industrial grade 20° Baume HCl.
2. Hooker Electrochemical Company, Niagara Falls, New York
Showed only mild interest, no price offering.

CHLORINE, Cl₂

The following companies showed interest in the production of chlorine at the Arsenal:

1. Frontier Chemical Company, Wichita, Kansas
Offered \$35.00 a ton, f.o.b. Denver in Frontier's railroad cars, for entire output from Arsenal.

2. Hooker Electrochemical Company, Niagara Falls, New York
Showed considerable interest in purchasing chlorine but made no price offering.
3. Columbia-Southern Chemical Corporation, Pittsburgh, Pennsylvania
Showed considerable interest in chlorine and calcium chloride but made no price offering.

CHLORINE OR ANY CHLORIDE

The following companies were contacted concerning the production of all possible forms of chlorine or chlorides from the Arsenal and showed no interest in any of the possible products:

1. Allied Chemical and Dye Corporation
 - a. Solvay Process Division
 - b. General Chemicals Division
2. Dow Chemical Company
3. E. I. du Pont de Nemours & Company, Inc.
4. Stauffer Chemical Company
5. Diamond Alkali Company
6. Wyandotte Chemical Company
7. Westvaco Chlor-Alkali Division of Food Machinery Corporation

ALUMINUM CHLORIDE HYDRATE

The following companies were contacted specifically about the purchase of aluminum chloride hydrate and despite the fact that they are the major producers of anhydrous aluminum chloride, showed no interest in purchasing the hydrate:

1. E. I. du Pont de Nemours & Company, Inc.
2. Hooker Electrochemical Company
3. Elberta Chemical Company

REMEDIAL MEASURES

REDUCTION OF WATER WASTE

The volume of water used and discarded in both the Chemical Corps' and Shell's plants can and should be reduced to a minimum as soon as possible and independently of any other action.

At the recommendation of The Ralph M. Parsons Company, pumps are being installed and the necessary piping changes being made so that the water required for the steam jet barometric condensers in Plant No. 1 can be recirculated over the cooling tower, instead of being used "once through" and drained to the contaminated lake. This modification to the plant is expected to reduce the water usage and wastage by more than 50 per cent, or 10 million gallons a month at present levels of operation.

Negotiations can and should be initiated with Shell Chemical Company:

1. To require that Shell reduce the volume of their plant effluent to a practical minimum. This requirement could involve the installation of a cooling tower by Shell to recirculate all of the cooling water that is now being dumped to the contaminated lakes.
2. To require that Shell install a flow measuring device (a flume and weir would be satisfactory) with a permanent flow recorder and divert all of their effluent streams through this device.
3. To require Shell to report daily average flow and chemical analysis of effluent to the contaminated lake.

TEMPORARY DISPOSAL OF DISSOLVED SOLIDS

As will be pointed out in later sections of this report, a permanent system of disposal of the chemical wastes produced by the various plants at full production will require considerable time for installation. Temporary provision for the disposal of these wastes can be made relatively rapidly by installing a water-tight seal on the bottom of reservoirs and containing these waste streams for solar evaporation of the water.

Present operation of Plant No. 1 is at a considerably lower rate than the maximum plant capacity for which permanent waste disposal facilities must be provided. After the necessary changes have been made in Plant No. 1 to recirculate the cooling water used in the steam jet barometric condensers, and with the instigation of water conservation programs in the various plants, it appears *has this been done?* entirely possible to limit the total volume of effluent from all plants to an average of less than 150 gpm. This average flow is based on the assumption that Shell can make some changes in their plant to reduce the volume of effluent from their plant to 50-70 gpm and that the average flow from Plant No. 1 can be reduced to 50-70 gpm. The reduction of average effluent from Plant No. 1 to this low level would have to be accomplished by operation of the plant only a part of the time. To illustrate this point, an instantaneous discharge of 200 gpm would be satisfactory if the plant were operated only 25 to 30 per cent of the time. *F*

Data obtained from the United States Department of Commerce, Weather Bureau Records, show an average evaporation rate of water in the Denver area of 47* inches a year, exclusive of rain and snowfall. Using an average value for precipitation of 14 inches a year, the net calculated loss of water from open ponds would be 33 inches a year. This is equivalent to about two gallons of water a minute lost from an acre of pond area. To give a margin of safety, the pond area required will be based on 1 gpm of evaporation per acre. To dispose of the minimum total discharge from all the plants, a sealed reservoir area of about 150 acres will be required.

Our measurements of the area of the following existing reservoirs is as follows:

Reservoir "C"	-	67 acres
Reservoir "D"	-	8 acres
Reservoir "E"	-	22 acres
Reservoir "F"	-	<u>45</u> acres

Total 142 acres

All four reservoirs should be sealed to provide sufficient capacity for the effluent volume assumed above. The location of these reservoirs and the necessary ditches and canals is shown on Drawing No. 1113-AD7 at the end of this report.

* No data available for five winter months so loss for this period extrapolated from summer data.

Cost of Sealing Reservoirs

In the course of our study of methods for sealing the bottoms of reservoirs, the Bureau of Reclamation was contacted for advice and suggestions on this problem. Mr. Walter Price* commented that a bentonite seal should be effective for this service and might be the most economical material to use. He pointed out that a similar study had been made by the Bureau in 1942 for a caustic storage pond. Apparently, in that proposed service of lining the caustic pond, the 50 per cent caustic to be stored would have had a strong dehydrating effect on the bentonite and thus prevent a seal from forming. The brine to be stored in this new service should not act in this manner and therefore chances for a good seal are better.

There are a number of factors in the use of bentonite which could not be determined at this time. A survey would have to be made to determine the nearest source of a suitable clay for this purpose. Tests would have to be conducted to determine the effectiveness of bentonite for storing this brine and the thickness of the clay layer required to insure a tight seal. These determinations could probably best be made by the Bureau of Reclamation.

The use of a sprayed catalytically-blown asphalt membrane, protected by a layer of dirt, gravel, asphaltic concrete, et cetera, is a relatively widely used technique for sealing reservoir bottoms. This membrane generally gives excellent service and long life. Failures have occurred in some installations usually due to faulty sub-grade preparation or asphalt application. Inspection of the installation is difficult as the physical appearance of the asphalt layer can be good whether the layer is a proper 3/8 inch thick or merely a very thin coat. However, with good supervision and proper care, the installation can be practically perfect.

The cost of installing sprayed and brined asphalt membrane to seal the bottoms of the four reservoirs listed above and totaling approximately 142 acres and the necessary ditches and canals is estimated to be \$667,000. A breakdown of these costs is given on Table III.

In the preparation of this estimate it was assumed that Reservoir "C" would have to be excavated to an average of one foot deeper than it is presently to get to a subgrade with sufficient bearing strength to support heavy equipment and yet retain the smooth finish grade required for the membrane application. The cover

* Chief, Division of Engineering Laboratories, Bureau of Reclamation, Denver Federal Center, Denver, Colorado

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material would be fresh "borrow" from the surrounding area.

A considerable amount of excavation would have to be done to prepare the ditches and canals for lining. A very shallow slope would be required on ditch sides to keep the protective cover from sloughing off.

In all cases, we have assumed that the application of 2 gallons of asphalt per square yard would be satisfactory and that the proper grade of asphalt would have to be shipped into the Denver area from major petroleum refining areas 1,000 miles away. If further insurance of a perfect seal is desired, the thickness of the asphalt layer can be increased to 3 or even 4 gallons per acre, at a correspondingly higher cost. In our opinion, however, proper attention to insure a good installation would result in a satisfactory seal at the most reasonable cost.

The use of prefabricated asphalt panels was considered for this application as this technique would probably insure a more impermeable seal of the reservoirs. However, the cost of such an installation was estimated by Globe Engineering Company using Envoy Petroleum Company's panels to be \$0.33 per square foot on a prepared subgrade, or about 3 times the cost of a sprayed asphalt membrane.

TABLE III

ESTIMATED COST OF INSTALLATION OF ASPHALT MEMBRANE
UNDER RESERVOIRS FOR ROCKY MOUNTAIN ARSENAL

<u>Description and Units</u>	<u>Quantity</u>	<u>Unit Cost \$</u>	<u>Cost Ext. \$</u>	<u>Total Cost \$</u>
Reservoir "D", 8 acres				
Reservoir "E", 22 acres				
Reservoir "F", 45 acres				
Blading (Level grading) sq.yd.	363,000	0.08	29,000	
Asphalt membrane lining, gal.	726,000	.22	160,000	
Blanket backfill, cu.yd.	121,000	.55	<u>66,600</u>	
Total				255,600
Reservoir "C", 67 acres				
Grade off 1 ft. and waste, cu.yd.	108,200	.40	43,300	
Asphalt membrane lining, gal.	649,000	.22	143,000	
Blanket backfill (borrow) cu.yd.	108,200	.50	<u>54,100</u>	
Total				240,400
Canals, 11,500 lineal feet Rehabilitate Sand Creek Lateral				
Excavation 1 ft. stockpile and re-use, cu.yd.	5,540	2.00	11,100	
Asphalt membrane lining, gal.	34,000	0.22	7,500	
Backfill, added rock and compacted, cu.yd.	5,540	1.50	<u>8,300</u>	
Total				26,900
Ditches, 7,500 lineal feet Rehabilitate existing				
Excavation 1 ft. stockpile and re-use portion, cu.yd.	6,670	1.75	11,700	
Asphalt membrane lining, gal.	22,200	0.22	4,900	
Backfilled, added rock and compacted, cu.yd.	6,670	1.50	<u>10,000</u>	
Total				26,600

TABLE III (Cont'd)

<u>Description and Units</u>	<u>Quantity</u>	<u>Unit Cost \$</u>	<u>Cost Ext. \$</u>	<u>Total Cost \$</u>
Ditches, 3,500 lineal feet New				
Excavation, cu.yd.	3,120	1.90	5,900	
Asphalt membrane lining, gal.	10,360	0.22	2,300	
Backfill, added rock and compacted, cu.yd.	1,685	1.50	<u>2,500</u>	
Total				10,700
TOTAL BASIC CONSTRUCTION COST				\$560,200
Contingencies	10%		\$56,020	
Engineering and Supervision	9%		50,418	
Sub-total				<u>106,438</u>
TOTAL ESTIMATED PROJECT COST				\$666,638

CLEAN-UP OF HYDROGEN CHLORIDE FROM PLANT NO. 1

Need for the Clean-up

The basic philosophy of our approach to the problem of the disposal of chemical wastes is to convert these waste chemicals to materials which are saleable and for which a market exists.

Our survey indicates that markets exist for chlorine and some hydrochloric acid, with chlorine being the only chemical for which the market is diversified and large.

Commercial users of hydrochloric acid have not established purity specifications covering phosphorus and fluorine as these are not normal contaminants in hydrochloric acid. Discussions with acid marketers indicate, however, that these contaminants should be practically completely excluded for the acid to have a ready market.

In converting hydrogen chloride to chlorine by any of the known processes, the effect of the contaminants, phosphorus and fluorine, is unknown. Neutralization of the crude acid followed by electrolysis of the brine to produce chlorine might result in a number of difficulties:

1. The caustic scrubbers in the plant salt up and plug very rapidly if it is attempted to produce a brine stronger than 5 to 10 per cent. This dilute brine could seriously effect cell efficiency and would be likely to shorten anode and diaphragm life considerably.
2. Recycling of the caustic cell liquor to the scrubbers for further acid neutralization and brine production would permit a build up of impurities. There is no known method for separating the impurities from a sodium chloride solution.
3. Present operation of the scrubbers requires an excess of caustic be used to insure decontamination of the gases. This excess caustic must be neutralized before the brine is electrolyzed if good cell efficiency and life is to be obtained.

The Grosvenor-Dow process for production of chlorine from hydrogen chloride is catalytic rather than electrolytic. The acid feed gas to this process must be pure to insure long catalyst life.

Recovery of Valuable Impurities

1. By Refrigeration: Purification of the by-product hydrogen chloride gas from Plant No. 1 can be accomplished most readily by greatly reducing the temperature of the acid gas streams before they leave the main process. These temperatures can be reduced by increasing condenser surface area and refrigeration capacity. This would result in the recovery of enough of the Plant No. 1 product to increase efficiency 6 to 8 per cent.

The Step IV off-gas is presently cooled to 83-90° F by a circulating methylene chloride liquid stream at 77° F. This condensing system was designed for a condensate which would solidify at about 80-90° F. In normal operation at present, the off-gas scrubber is completely or partially by-passed. When this is done, the phosphorus compound taken off in the hydrogen chloride gas is many times more volatile than the compound for which the unit was designed and has a freezing range between -30 and -40° F.

It is recommended that a second condenser be installed on the acid gas streams after each of the existing Step IV off-gas condensers in each of the three bays. This new condenser would be chilled by the existing 10° F methylene chloride stream. Our design (see Flow Sheet No. 1113-AE4 at the end of this report) calls for a unit which would reduce the off-gas temperature to 25° F.

The condensers in Step V have no excess capacity over the original design production rates. At the higher rates contemplated, they will be considerably undersized. The off-gases from the Degas and the Distillation condensers are presently cooled to between 45 and 80° F, (depending on production rate) using the 10° F methylene chloride liquid as the cooling medium.

It is recommended that the existing condensers in each bay be replaced with considerably larger units and that a much colder refrigerant be used for cooling. These existing condensers cannot be kept in service and merely supplemented with other condensers in series because the pressure drop (at high production rates) across the existing units is too large to permit the installation and operation of acid recovery equipment on these gas streams.

Our design (see Flow Sheet No. 1113-AE4) calls for condensers to cool the gas streams to -40° F using direct expansion of Freon at -50° F in the condenser tubes. This system will require the addition of a refrigerating machine with a capacity of about 200 tons at -50° F for operation of three bays at the specified full

production rates.

These modifications and additions to the existing plant will reduce the loss of phosphorus compounds in the acid off-gas from an estimated 10,000 pounds a day at full production rates in the present plant equipment to something less than 1,000 pounds a day.

2. By Compression and Condensation: It appears to be entirely feasible to use a mechanical vacuum pump on the off-gases from Step V instead of the presently used steam jets. Piston compressors made of cast iron give excellent service pumping anhydrous hydrogen chloride in many chemical plants. With certain precautions a cast iron vacuum pump should operate successfully on the Step V off-gas.

The only apparent hazard in this scheme is from the occasional introduction of water into the system. The presence of even minute quantities of water in the hydrogen chloride would cause rapid and severe corrosion of the cast iron vacuum pumps.

Water is put into the reaction system to wash down and decontaminate the equipment prior to maintenance. At such a time, however, the vacuum pump would not be running and could be valved off.

During start-up, while some water is in the system, the existing steam jets should be used to reach operating pressures before the flow is switched to the vacuum pump to maintain the desired low pressure. This start-up procedure avoids two problems:

- a. The motor horsepower required for the pump will be minimized.
- b. Any water vapor in the vent lines will be swept out and replaced with process gases, some of which should be excellent dessicants.

Compression of these off-gases would permit practically complete recovery of the product and valuable reactants presently being lost in the off-gas stream. Our calculations show that the use of a mechanical vacuum pump would permit the recovery of 500 pounds a day more of these materials than would be recovered using refrigeration alone. Therefore, despite the high initial cost of the vacuum pump, about \$500,000, the economics would favor such a scheme.

We, therefore, recommend that pilot scale tests be run on the use of a cast iron piston vacuum pump to maintain the required low pressure in the Step V Degas and Distillation section of the plant.

These tests could be conducted in the present plant relatively cheaply. A satisfactory test program would be as follows:

- a. Tap into the existing Hastelloy vent line from Step V Degas or Distillation Columns and install a Hastelloy block valve.
- b. Connect the suction of a cast iron vacuum pump to this take-off.
- c. Return the discharge of the vacuum pump to the vent line through a pressure control valve and a Hastelloy block valve.
- d. When the operating pressure (vacuum) has been reached using the steam jets, start the vacuum pump and determine for how long the pump can maintain its differential pressure. The pump would have to be fitted with a gas seal using "bone-dry" air or nitrogen in the seal to prevent leakage of wet atmospheric air into the pump.

3. By Absorption in an Inert Solvent: The use of an inert wash solvent to scrub the desirable constituents out of the hydrogen chloride off-gas was considered and discarded. An efficient absorption system cannot be made to operate efficiently on a gas at the low pressure of the Step V off-gas.

Final Purification of Hydrogen Chloride

After the recovery of as much as possible of the valuable constituent in the by-product acid gas stream, further purification will still be required if the acid is to be sold or converted to chlorine. This final purification is accomplished by absorption of the crude gas in water, followed by distillation and finally re-absorption of the pure hydrogen chloride.

Our design (see Flow Sheet No. 1113-AE₁) calls for the absorption of the Step V acid gas in a recycled weak acid of about an azeotropic mixture to minimize vaporization of the absorbent. The acid strength increases from about 20 per cent to about 27 per cent in the vacuum absorber. The 27 per cent acid is then pumped to the atmospheric absorbers where the Step IV off-gas is absorbed. The resultant acid from the atmospheric absorbers is about 32 per cent by weight HCl. Identical absorption systems are specified for each of the three main processing lines and this equipment will be inside the main processing building.

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The strong (32%) acid from each of the three parallel absorption systems is pumped to a common surge drum outside of the processing building for further processing as a single stream. The acid is pumped to the Primary Acid Distillation Column from which hydrogen chloride and water are the only overhead products. The bottoms products are the 20 per cent HCl-water azeotrope, hydrofluoric acid, isopropyl alcohol and methyl phosphonic acid.

The hydrogen chloride-water overhead product from the Primary Column is re-absorbed in water to form pure 20° Baume hydrochloric acid and stored in two 50,000 gallon rubber-lined steel tanks until sold. The gaseous or aqueous acid can also be further processed to produce chlorine.

The bottoms product from the Primary Acid Column is recycled to the acid absorbers. A portion of this bottoms stream is pumped to the Secondary Acid Column where most of the hydrochloric acid is taken overhead contaminated with hydrofluoric acid and recycled to the absorbers.

The bottoms product from this secondary column must be disposed of. It consists of isopropyl alcohol, hydrofluoric acid, methyl phosphonic acid and some hydrochloric acid.

It is estimated that the necessary equipment to refrigerate the entire volume of off-gases from Plant No. 1 at full production, and to convert this gas to pure acid, will cost \$2,050,000 (see Table IV). This estimate includes the costs of engineering, purchasing and construction of the facilities as given on the Process Flow Diagram No. 1113-AZ1, as well as the new 200 ton refrigeration machinery which is required. The condensers and absorbers shown on the Flow Diagram as being inside the building are to be installed inside the existing process building during a complete plant shutdown. The equipment shown as being outside is to be located in an asphalted area adjacent to the existing process building. No shelter is provided for this outside equipment. The new refrigeration equipment is to be installed in an existing building near the process building.

This proposed acid purification plant is estimated to produce 3000 tons a month of purified 20° Baume hydrochloric for \$6.21 a ton. A detailed breakdown of this production cost is given in Table V.

It should be noted that to attain reasonable operating flexibility, additional facilities will be required to convert the acid to a neutral brine and transfer it to the existing brine storage tanks

in the chlorine plant for evaporation and stockpiling as crystalline salt. These facilities are estimated to cost an additional \$144,500. The details of this cost estimate and of the equipment requirements are given in the section of this report entitled "Disposal of Purified Hydrogen Chloride", Method E, page 30.

The plant designed to perform the above purification is somewhat of a compromise over what could probably be done if more process information were available. The lack of information makes necessary the use of ample safety factors in order to be sure of having enough capacity in the plant. An extensive literature search was made to find data on the ternary system $\text{HCl-HF-H}_2\text{O}$, or on the three possible binary systems, $\text{HCl-H}_2\text{O}$, $\text{HF-H}_2\text{O}$ and HCl-HF . No data whatsoever were found on the ternary system nor on the HCl-HF binary. As expected, data were also lacking for the effect of isopropyl alcohol or of methyl phosphonic acid on this distillation system. We are relatively sure of the operation of the Primary Acid Column and the production of good quality acid. The capacity of this column is probably larger than is required.

The Secondary Column is the weakest part of the design. No column calculations could be made for the ternary system $\text{HCl-HF-H}_2\text{O}$. Furthermore, it was assumed that isopropyl alcohol forms its normal azeotrope with water and does not azeotrope with the methyl phosphonic or other acids. The operation of the Secondary Acid Column is not critical however, and we expect it to operate reasonably satisfactorily.

We strongly recommend that data be developed in the laboratory on the distillation of this mixture prior to the final design and installation of this plant. The cost of such a program should be under \$5,000 and would possibly save many times this amount in the final cost of the plant.

Until these missing data are developed, no guarantees can be made of the production capacity of the plant or of the quality of the products.

TABLE IV

ACID PURIFICATION PLANT
INVESTMENT COST ESTIMATE

Basis: Plant to be added to existing Plant No. 1 to recover, and return to process 8 to 10,000 lbs. a day of phosphorus compounds presently being lost in acid off-gas streams, and to produce 3,064 tons/month of pure 20° Baume hydrochloric acid from the off-gases of Plant No. 1 at full production.

Basic Plant Cost	\$1,693,000
Contingency 10%	<u>169,000</u>
PLANT CONSTRUCTION COST	\$1,862,000
Process Design	10,000
Field Check of Existing Plant	10,000
Architect-Engineer Design	
(Rehabilitation and New Facilities) 5.9%	110,000
Administration, Inspection and	
Supervision 3.1%	<u>58,000</u>
TOTAL PROJECT COST	\$2,050,000

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TABLE V

ACID PURIFICATION PLANT

PRODUCTION COST ESTIMATE

Basis: Separation of waste gases from Plant No. 1 to get pure HCl gas which is absorbed in water to form 3,064 tons/month of 32.5 weight per cent acid.

Investment				
Process			\$2,050,000	
<u>Raw Materials</u>	<u>Basis</u>	<u>Units/Mo</u>	<u>\$/Mo</u>	<u>\$/Mo</u>
Waste Plant Gases	tons	1,046	--	
Total				--
<u>Utilities</u>				
Steam	\$ 0.63/M lb	7,100	4,480	
Electricity	10.00/M kwh	280	2,800	
Water	0.02/M gal	70,000	<u>1,400</u>	
Total				8,680
<u>Processing</u>				
Labor and Benefits	2.55/MH.	1,125	2,865	
Supervision			460	
Repairs (labor)	2.68/MH	675	1,810	
Supplies			<u>1,800</u>	
Total				6,935
<u>Non-Processing</u>				
Gen. Admin. and Office	10% of Processing		694	
Miscellaneous	40% of Processing		<u>2,770</u>	
Total				<u>3,464</u>
<u>GROSS PRODUCTION COST</u>				19,079

Gross Acid Cost = $\frac{\$19,079}{3,064} = \$6.21/\text{ton}$

DISPOSAL OF PHOSPHORUS RESIDUES FROM PLANT NO. 1

Results of tests conducted under the supervision of Dr. Arthur S. Newman showed that methyl phosphonic acid can be toxic to plants. Chemical analysis of the water from a well on Arsenal property shows that methyl phosphonic acid can move with the underground waters. Therefore, it seems important to keep solutions of this material from getting into the underground water supply. The only practical method for converting methyl phosphonic acid to a non-toxic phosphate is to heat to 1000° F or higher. The only other disposal technique that can be used would be to lagoon this waste stream in a sealed reservoir.

Recommendations

The alternatives in the disposal of phosphorus residues from Plant No. 1 are stated here, together with the recommended course of action for each:

1. If the only phosphorus residues to be discarded are those contained in the bottoms from the Secondary Acid Column, discussed previously, and the recommended new condensers and refrigeration equipment are installed, the total phosphorus wastes will amount to considerably less than 1000 pounds a day. This quantity would not be enough to warrant processing and should be pumped to the sealed lake.
2. If the residues from the Final Stripper of the main process are to be discarded in addition to the residues from the Secondary Acid Column, the quantity of phosphorus wastes will amount to over three tons a day. This larger quantity is probably too much to send to the sealed lake and should be converted to phosphates.

The conversion of methyl phosphonic acid to calcium phosphate is accomplished as follows:

1. Decontaminate the Final Stripper residues with water in the existing decontamination tanks.
2. Combine the residue in the decontamination tanks with the residue from the Secondary Acid Column.

3. Pump the mixture to the Blending Tanks, T-1, T-2 or T-3 shown on Flow Diagram Calcium Phosphate Fertilizer Plant Drawing No. 1113-AE2, and neutralize the acid stream with excess crushed limestone.
4. The limestone and neutralized acid slurry is fed to a roaster and calcined in an oxidizing atmosphere at 1500° F. This heating converts the feed mixture to a crude calcium phosphate containing excess lime.
5. The crude phosphate is then cooled and stock-piled for future sale.

A detailed discussion of the calcium phosphate plant follows:

Calcium Phosphate Fertilizer Plant

The crushing section of this plant is designed for 6 inch rock or smaller. Larger rock would greatly increase the cost of this portion of the plant as it would necessitate two stage crushing in order to reduce the feed to the 1/2 inch size required for the ball mill. In a plant with the small capacity of this one, the feed lump size to the crusher, and not the capacity, is the controlling factor in the size of the machine.

Crushed rock storage has been eliminated to minimize the capital cost of the plant as this eliminates the need for additional conveyors and feeders. This does require continuous operation of the hammer mill, but due to the small capacity, maintenance will not be excessive. Incoming raw limestone rock would be dumped directly into the crusher feed bin by the vendors trucks, after the storage pile and ramp has been built up to required height and capacity. This pile would only be used in case of non-delivery of limestone. Three ten-ton loads per day will charge the bin under normal conditions.

In order to maintain continuous operation of the rotary kiln, two blending tanks have been specified with a total storage capacity of 4 hours plus one hour reserve in kiln feed tank. Five hours capacity ahead of the kiln should be ample time for changing or reversing hammers, liners, et cetera, in the hammer mill.

The grinding section (1/2 inch to 80%-100 mesh) should operate continuously for months. It is estimated that the ball consumption will amount to about 1-1/2 to 2 pounds per ton of feed. Ball storage of 3 tons has been provided adjacent to the mill.

The standard dust chamber has been provided for the kiln without additional dust collectors. The collected dust from this chamber is sucked out into the suction inlet line to the kiln draft fan and blown up the stack. If this is found to create an undesirable dust condition in the plant area, space has been provided for the installation of a Multiclone collector, or a scrubber, next to the above chamber. The collector or scrubber would be served by the same kiln draft fan, with a minimum change in the fan suction line.

The finished product is piled by a belt stacker, moving in an arc of 40°. The pile has triangular cross section, being 21 feet high at the apex with a base of 60 feet. This gives a storage of about 1080 tons, or 60 days storage. Two 100 feet lengths of garden hose with a "fog nozzle" are provided to keep the surface of the pile damp enough to prevent dust loss. If it should be found necessary to add additional hoses, this can easily be done. A 1-ton payload is provided for loading from the product pile into trucks. If the limestone delivery trucks should not be in operation, due to strikes or bad weather, the payload would be used to load lime rock into the crusher feed bin from limestone storage, which would take about 3 hours.

It should be understood that if the market later requires a finished product of uniform size, an additional small crushing, screening and bag packing plant would be required, to be placed ahead of the final stockpile.

It is estimated that design, purchasing and construction of this plant, to dispose of up to 10 tons of methyl phosphonic acid (dry basis) a day, would cost approximately \$640,000. The breakdown on this cost is as follows:

Direct Construction Cost	\$453,650
Construction Contractor's Overhead 10%	<u>45,350</u>
Sub-total	\$499,000
Contingency 10%	<u>49,900</u>
Sub-total	\$548,900
Construction Contractor's Profit 7%	<u>38,100</u>
TOTAL CONSTRUCTION COST	\$587,000
Engineering and Supervision 6%	35,000
Administration 3%	<u>18,000</u>
TOTAL PROJECT COST	\$640,000

DISPOSAL OF HYDROGEN CHLORIDE

Dicussion

The results of our survey indicate that a market exists in the Denver area for an average daily quantity of about 50 tons of 20° Baume hydrochloric acid. If the production from Plant No. 1 is limited so that the by-product acid production is less than 50 tons a day, the production and sale of this acid, as such, is clearly the least expensive program for disposal. If, however, the production of Plant No. 1 reaches the rate presently considered to be the maximum, much more than 50 tons of acid must be disposed of daily. In this case, the only method for which data is available for getting rid of the surplus of acid would be neutralization with caustic soda to form a sodium chloride brine, followed by either electrolysis to produce chlorine, or crystallization and stock piling of the solid salt.

If the salt is stock piled and production continues, eventually enough salt will accumulate to justify or force full scale operation of the existing chlorine plant to electrolyze the salt to chlorine. The stock of salt will be used up, electrolytic operations will stop, and stock piling will be started again. Thus, pending receipt of data from Hercules Powder Company, the long range alternatives for taking care of the salt from the surplus acid are that it shall be either continuously or intermittently electrolyzed to chlorine and caustic.

The five principal methods for disposing of the by-product hydrogen chloride from Plant No. 1 are described and evaluated in the following pages.

Method A, Present Disposal Method: The crude hydrogen chloride gas streams are not purified, but are absorbed directly in dilute caustic soda solutions in gas scrubbers. An excess of caustic is used and the alkaline brine that results is pumped to the contaminated lakes. In Table VI on page 31 the operating costs by this method are estimated to be \$63,600 a month for the assumed full Plant No. 1 production rate. As almost all of the operating cost by Method A is in the caustic soda used, the monthly cost can vary considerably with changes in operational procedures. The calculated cost of this method is based on the present (June 1955) plant usage of 140 per cent of theoretical required for exact neutralization.

Method B, Continuous Electrolysis to Chlorine and Caustic: The purified hydrogen chloride, in the form of a strong aqueous acid, is exactly neutralized with dilute caustic soda solution. The pure

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NaCl brine is pumped to the existing chlorine plant and electrolyzed.

At the assumed operating rate, 1,090 tons/month of NaOH reacts with 996 tons HCl to form a 15 per cent brine composed of 1,600 tons NaCl and 9,060 tons of water. This brine is pumped through a new pipeline to the cell liquor storage tanks in the chlorine plant at an average rate of 64 gallons a minute.

The salt is converted to chlorine and caustic soda generally using 100 cells or about 1/4 the capacity of the existing electrolytic chlorine plant. To match this small load, the capacity of the evaporator system is reduced by using only one evaporator body. 100 cells will not take care of all the salt, so periodically another line of 100 cells must be added and used until the accumulated salt surplus is consumed.

The chlorine produced is sold and the caustic is periodically returned to the Plant No. 1 caustic storage tanks through the same pipeline as used for the brine.

The operating costs by this method are estimated at \$90,500 a month. See Table VII on page 32. This includes a charge of \$6.21 a ton for the purified aqueous hydrochloric acid (see Table V on page 23) allowing credit for the chlorine and caustic. The investment required is estimated to be \$2,747,000.

Brine could be conveyed to the chlorine plant by tank cars. The initial investment would be smaller; i.e., about \$8,000 to give ten tank cars a corrosion resisting coating, but the much larger operating cost would make this the more expensive method within two years.

Method C, Evaporation and Stockpiling of Salt: The process for Method C is the same as for Method B up to the point where the brine is received in the cell liquor storage tanks of the chlorine plant. The fifteen per cent brine is then evaporated in the existing evaporator to produce a slurry of crystalline salt. An automatic batching centrifuge is to be installed to dewater the crystalline salt, which is to be stored outside on the existing concrete slab. If Plant No. 1 continues to run at the assumed rate for more than a year, another concrete slab will be built to increase the outdoor storage capacity to take care of a total of three years output of salt. The new slab, like the existing one, will be designed to allow the salt to be removed from storage as a brine.

The process steps and equipment required are illustrated in the Flow Diagram for Method C, Drawing 1113-AE5, placed at the end of this report.

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The operating costs by Method C are estimated at \$95,200 a month (Table VIII on page 33). About two-thirds of this cost consists of the charges for the caustic and the pure aqueous HCl. No credit is allowed for the salt since none of it is expected to be sold. The process investment is estimated to be \$3,056,900 including the supplementary investment of \$195,400 to be made after about twelve months of operation to add another storage slab and extend pipelines and conveyors.

It is important to note that, while the salt from the Sharples centrifuge will be dry enough to be conveyed to outside storage, it will need to be kiln dried if it is to be sold for any of the more common salt uses. The necessary drier, storage silo, and conveyors are estimated to cost \$66,400 installed. The limited local market for the salt (see Market Survey section of this report) does not justify this investment, so the cost of the kiln drying equipment is omitted from the process investment for Method C as shown in Table VIII.

Method D, Catalytic Conversion to Chlorine: This process has been developed by Hercules Powder Company in a small commercial plant with about the same capacity as is needed to take care of the assumed rate of HCl production from Plant No. 1. In Method D the stream of purified HCl gas will go through a low temperature drying operation instead of being absorbed in water as in Methods B and C. The dry gas then is absorbed by ferric oxide in the first Hercules process reactor, producing ferric chloride. The ferric chloride is moved to the second Hercules process reactor where it is oxidized by air or oxygen to yield chlorine gas and ferric oxide.

Tail gases from the first reactor will go through a new scrubber in which caustic will remove the last traces of HCl. The salt in the brine from this final scrubber is assumed to amount to about 2 tons/day. The brine from all these scrubbers will be pumped to the contaminated lake.

The chlorine from the Hercules process will be recovered by low temperature liquefaction and sold as liquid chlorine.

The process investment for the chlorine plant is estimated by Hercules Powder Company to be \$1,350,000 and to produce chlorine for \$34.66 a ton (See Table IX, page 34). The total investment for this disposal scheme is estimated to be \$4,067,000.

Hercules has been operating this plant for about two years on an experimental basis. They have indicated that the process has now

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been firmed up and most of the "bugs" eliminated. A detailed cost breakdown has been promised us within the next few months. Our analysis of their data and recommendations on the application of this process to the problem at Rocky Mountain Arsenal will be submitted as a supplement to this report.

Method E, Sale of Acid, Stockpile Surplus as Salt: Method E is a variation of Method C in which a large portion of the pure hydrochloric acid is sold as acid. Only the residual unsold acid is converted to brine, evaporated, and the salt stock-piled.

The present market capacity for hydrochloric acid in the area is estimated to be 1500 tons/month of the 31.2 per cent grade, (468 tons anhydrous HCl). The surplus (equal to 528 tons anhydrous HCl) is neutralized with 578 tons NaOH (100% basis) to form 846 tons NaCl in a 15 per cent salt brine. Evaporation of 4,768 tons/month of water is required.

With this smaller evaporation load, it may be more economical to fill all the available storage capacity of the chlorine plant with brine from Plant No. 1 before starting up an evaporator, then to run the evaporators at the maximum rate, using all the effects, until the stored brine is exhausted.

The equipment for Method E is the same as for Method C, except that two automatic batching centrifugals may be needed to dewater the salt crystals when the evaporator plant is run at full capacity. The process investment is therefore increased by the estimated installed cost of one centrifugal. The operating cost by this method is estimated to be \$51,700 a month, allowing a credit for the acid sold at \$5.00 a ton of aqueous 31.5 per cent hydrochloric. There is a sizeable saving over other methods by the reduction in requirements for caustic (Table X, on page 35). The process investment is estimated to be \$2,861,500. After about 18 months operation at the assumed rate, the storage slab will be full and it will be necessary to make the same supplemental investment that Method C requires after 12 months.

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TABLE VI

DISPOSAL OF HYDROGEN CHLORIDE
 Method A: Absorption in Caustic,
 Brine Pumped to Contaminated Lake

OPERATING COST ESTIMATE

Basis: Present method. Absorption in caustic of crude gas containing impurities and 996 tons/month of HCl, followed by pumping dilute, alkaline brine to the contaminated lake.

Investment
 Process

Not estimated, probably small.

<u>Raw Materials</u>	<u>Basis</u>	<u>Units/Mo</u>	<u>\$/Mo</u>	<u>\$/Mo</u>
Caustic Soda, 50%	\$41.35/T*	1,505**	62,200	
HCl in Impure Gas	Tons	996	<u>n.c.</u>	
Total				62,200
<u>Utilities</u>				
Electricity	\$10.00/M kwh	10	100	
Water	\$ 0.02/M gal	15,400	<u>308</u>	
Total				408
<u>Processing</u>				
Labor and Benefits	\$ 2.60/MH	150	390	
Supervision			60	
Repairs (labor)	\$ 2.97/MH	40	119	
Supplies			<u>60</u>	
Total				629
<u>Non-Processing</u>				
Gen. Admin. and Office			102	
Miscellaneous	40% of Processing		<u>252</u>	
Total				<u>354</u>
<u>GROSS OPERATING COST</u>				63,591
Credits:			None	
<u>NET OPERATING COST</u>				63,591

* Dollars per ton of 100% NaOH contained in solution.

** Assuming usage of 140% of theoretical.

TABLE VII

DISPOSAL OF HYDROGEN CHLORIDE

Method B: Neutralization of Pure Aqueous Acid by
Caustic Followed by Electrolysis of Salt to Chlorine and Caustic

OPERATING COST ESTIMATE

Basis: Pure aqueous hydrochloric acid containing 996 tons/month
HCl is neutralized with caustic to form 15% neutral brine,
followed by electrolysis to Cl₂ and NaOH in 100 or 200
cells of existing chlorine plant. Average production of
970 tons chlorine and 1,090 tons NaOH.

Investment				\$2,747,000
Acid Purification Plant	\$2,050,000			
Brine Transfer System	30,000			
Sealed Reservoirs	667,000			
<u>Raw Materials</u>	<u>Basis</u>	<u>Units/Mo</u>	<u>\$/Mo</u>	<u>\$/Mo</u>
Caustic Soda, 50%	\$41.35/T*	1,090	45,200	
HCl Acid, Aqueous, 32.5%	\$ 6.21/T	3,064	19,079	
Sulfuric Acid	\$27.00/T	17.5	473	
Total				64,752
<u>Utilities</u>				
Steam	\$ 0.63/M lb	15,000	9,450	
Electricity	\$ 7.30/M kwh	2,640	19,300	
Water	\$ 0.02/M gal	150,000	3,000	
Total				31,750
<u>Processing</u>				
Labor and Benefits	\$ 2.59/MH	9,900	25,650	
Supervision	\$ 4.06/MH	900	3,656	
Repairs (labor)	\$ 2.77/MH	3,650	10,100	
Supplies			7,325	
Total				46,731
<u>Non-Processing</u>				
Gen. Admin. and Office			7,364	
Miscellaneous	40% of Processing		18,700	
Total				26,064
<u>GROSS OPERATING COST</u>				169,297
Credits: Chlorine	\$35.00/T	970	34,000	
Caustic Soda	\$41.35/T	1,086	44,800	
Total				78,800
<u>NET OPERATING COST</u>				90,497

* Dollars per ton of 100% NaOH contained in solution.

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TABLE VIII

DISPOSAL OF HYDROGEN CHLORIDE

Method C: Neutralization of Pure Aqueous Acid by Caustic Followed by
Brine Evaporation and Stock-piling of Salt

OPERATING COST ESTIMATE

Basis: Pure aqueous hydrochloric acid containing 996 tons/month HCl is neutralized with caustic to form 15% neutral brine, followed by evaporation of the brine and stock-piling of the crystallized salt.

Investment				\$3,056,900
Acid Purification Plant	\$2,050,000			
Brine Transfer and Solids Handling	114,500			
Additional Storage	195,400			
Sealed Reservoirs	667,000			
<u>Raw Materials</u>	<u>Basis</u>	<u>Units/Mo</u>	<u>\$/Mo</u>	<u>\$/Mo</u>
Caustic Soda, 50%	\$41.35/T*	1,090	45,200	
HCl Acid Aqueous, 32.5%	6.21/T	3,064	19,079	
Total				64,279
<u>Utilities</u>				
Steam	0.63/M lb	16,300	10,280	
Electricity	10.00/M kwh	212	2,120	
Water	0.02/M gal	119,000	2,380	
Total				14,780
<u>Processing</u>				
Labor and Benefits	2.60/MH	2,700	7,020	
Supervision	4.02/MH	225	903	
Repairs (labor)	2.97/MH	675	2,000	
Supplies			576	
Total				10,499
<u>Non-Processing</u>				
Gen. Admin. and Office			1,480	
Miscellaneous	40% of Processing		4,200	
Total				5,680
<u>GROSS OPERATING COST</u>				95,238
Credits			None	
<u>NET OPERATING COST</u>				95,238

* Dollars per ton of 100% NaOH contained in solution.

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-22-55

TABLE IX

DISPOSAL OF HYDROGEN CHLORIDE
Method D: Oxidation to Chlorine by the
Grosvenor-Dow Process

OPERATING COST ESTIMATE

Basis: Conversion of 996 tons/month of purified HCl gas to chlorine by the Grosvenor-Dow (Hercules) process. Assume 96% conversion. 930 tons/month of chlorine liquefied and sold.

Investment		\$4,067,000
Acid Purification Plant	\$2,050,000	
Catalytic Chlorine Plant		
(estimate by Hercules)	1,350,000	
Sealed Reservoirs	667,000	
<u>Raw Materials</u>		
Caustic (to neutralize tail gas)		43.8 T/M
Pure HCl gas		996 T/M
<u>Utilities</u>		
Steam		2,680 M lb/Mo
Electricity		268 M kwh/Mo
Water		26,800 M gal/Mo

Hercules Powder Company estimates a production cost of \$34.66/T for chlorine produced at 50 T/D rate. Does not include overhead and indirect costs. This is about the selling price, f.o.b. Denver, for the liquid Cl₂ product. The cost would be slightly higher at a production rate of 996 tons/month, (37 T/D).

Estimated overall net operating cost for this system, (credit allowed for Cl₂ sold) not over \$10,000.

If Hercules' estimate did not include a charge for the pure HCl feed, add \$18,600 for 996 tons @ \$18.70/T.

TABLE X

DISPOSAL OF HYDROGEN CHLORIDE
Method E: Purified Hydrochloric Acid Sold
up to Capacity of Market. Excess Neutralized
and Stock-piled as Salt

OPERATING COST ESTIMATE

Basis: 996 tons/month of purified HCl gas absorbed in water to form 31.2% acid. 1,500 tons/month of acid sold, the rest neutralized to form salt brine, the brine evaporated and salt stock-piled.

Investment			\$2,861,500	
Acid Purification Plant	\$2,050,000			
Brine Transfer and				
Solids Handling	114,500			
Sealed Reservoirs	667,000			
<u>Raw Materials</u>	<u>Basis</u>	<u>Units/Mo</u>	<u>\$/Mo</u>	<u>\$/Mo</u>
Caustic Soda, 50%	\$41.35/T*	578	23,900	
HCl Acid, aqueous, 32.5%	6.21/T	3,064	19,075	
Total				42,079
<u>Utilities</u>				
Steam	0.63/M lb	8,640	5,440	
Electricity	10.00/M kwh	112	1,120	
Water	0.02/M gal	63,000	1,260	
Total				7,820
<u>Processing</u>				
Labor and Benefits	2.60/MH	800	2,080	
Supervision			250	
Repairs (labor)	2.97/MH	675	2,000	
Supplies			576	
Total				4,906
<u>Non-Processing</u>				
Gen. Admin. and Office			1,480	
Miscellaneous			2,910	
Total				4,390
<u>GROSS OPERATING COST</u>				59,195
Credits: Hydrochloric Acid	5.00/T	1,500		7,500
<u>NET OPERATING COST</u>				51,695

* Dollars per ton of 100% NaOH in solution.

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DISPOSAL OF ALUMINUM CHLORIDE HYDRATE AND HYDROGEN CHLORIDE FROM PLANT NO. 2

Plant No. 2 is presently in stand-by, so the purpose of this section of the report is to present a program for disposing of the by-products from this plant if and when it is started up again. This study was based on an assumed production rate from Plant No. 2 such that 669 tons of aluminum chloride (anhydrous basis) will be produced as a hydrate and 300 tons of hydrogen chloride will be produced monthly as by-products.

Dehydration of Aluminum Chloride Hydrate

Dupont and Hooker, both major producers of anhydrous aluminum chloride, were contacted in regard to any possible knowledge they might have had of processes to convert aluminum chloride hydrate to the anhydrous material. Both companies responded that they knew of no practical method for this conversion.

A report on this conversion prepared for the Chemical Corps by Gulf Chemical was reviewed. The process proposed in this report by Gulf for this conversion was unproved and untested. There were portions of the scheme that appeared very questionable to us. As a result of these factors, conversion of aluminum chloride hydrate to the anhydrous material was dropped from consideration.

Neutralization with Caustic

In the process we recommend for the disposal of the aluminum chloride hydrate and the hydrogen chloride from Plant No. 2, the by-product stream is neutralized with caustic soda. The resultant alumina floc is separated out as a solid and discarded. The brine produced by this reaction is to be pumped to the sealed reservoirs.

These by-product streams will be contaminated with phosphorus compounds. There are not sufficient data known on which to base a scheme for their removal. These contaminants could cause considerable trouble in a brine evaporation step, so it is desirable to initiate a laboratory program to develop a means for purification. Two techniques which might be applicable are:

1. Ion exchange, and
2. Fractional crystallization or precipitation

A laboratory program to develop this purification process could be started for a few thousand dollars. It is impossible to predict what the total cost of such a program might be.

The process we propose is based on the assumption that the phosphorus compounds would have to be separated out before recovery of the salt by evaporation could be attempted. A detailed discussion of the process is given in the next section.

Process Description

A filter cake of hydrated aluminum chloride and large amounts of hydrogen chloride gas are by-products from the Plant No. 2 operations. Nearly all the aluminum chloride and most of the hydrogen chloride come out of the process at the Bird continuous centrifugals.

The proposed chloride recovery process is shown in Drawing No. 1113-AC6, at the end of this report. An alkaline salt brine is sprayed under the Bird centrifugals to wash the $AlCl_3$ cake down into the existing sump and dissolve it. This spray also absorbs the HCl gases. A new and larger collecting sump receives the brine from the existing sump and also receives brines continually overflowing or periodically dumped from a scrubber, an air-washer, and a Nash vacuum pump. When the batch-operated pressure filters are cleaned out, alkaline brine is used to wash the filter cake into the new sump.

Caustic soda, some from recycle and some from make-up, is added to the new sump to hold the required degree of alkalinity. The aluminum chloride precipitates as a hydrated aluminum oxide, leaving sodium chloride and excess caustic in solution. The thin slurry mixture is pumped with a diaphragm pump to the top one of three paddle agitated tanks arranged in a cascade. The alumina crystals are fragile and easily broken up to produce a slime, therefore only mild agitation can be used if the solids are to have the proper settling characteristics. The crystals are aged and allowed to grow while moving down through the series of tanks. The thin slurry then flows into a rake classifier in which the denser alumina crystals settle and are raked out into a rotary drum filter. The alkaline salt brine, containing some finer alumina crystals, overflows from the classifier to a brine surge tank, from which some brine is recycled to the Bird centrifugals, and some overflows to a clariflocculator. The settled and thickened floc from the clariflocculator is pumped by a diaphragm pump into the rotary drum filter mentioned above. The filtrate from this filter returns to the feed trough of the clariflocculator. The alumina cake from the filter falls continuously into a screw conveyor which drops it just outside the processing area at the rate of 1,760 pounds per hour or 528 tons/month. From here the

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alumina is periodically scooped up and hauled away by dump truck to disposal in an area where drainage is toward the contaminated lake. The alumina cake has only a small percentage of chlorides in it, but since the behaviour of the water-soluble phosphorus compounds in this system is not known, it seems necessary to provide for the possibility that the cake may contain undesirable phosphorus compounds.

The overflow from the clariflocculator is an alkaline salt brine. This is clarified by filtering it through sand filters and it is then pumped to the ditch leading to the sealed reservoirs. The volume of this stream is estimated to be 64 gpm.

The estimated investment for the required additions to Plant No. 2 is \$195,750. This includes design, purchase and construction of the facilities shown on Flow Diagram No. 1113-AC6, plus the normal 10 per cent contingency.

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In addition to the major by-product streams of hydrogen chloride from Plant No. 1 and aluminum chloride hydrate from Plant No. 2, there are numerous minor by-product streams which must be disposed of. The source of some of these streams are principally as follows:

1. The remaining effluent stream from Shell Chemical Company's operations after provisions are made to recirculate the condenser cooling water. The solids content of this stream is calculated by Shell to be 4.4 tons a day of sodium sulfate and sodium acetate. It is not known to what extent Shell can reduce the volume of water discharged below the present level of 104 gpm.
2. If the phosphorus residues from Plant No. 1 are not large enough to warrant the installation of an incineration plant, these wastes must still be disposed of without risking the danger of underground water pollution.
3. The residues from the Mustard gas and white phosphorus plants are not large enough to convert economically to saleable or re-usable products. These also must be disposed of.
4. Waste water from equipment and floor decontamination and washdown from Plant No. 1. The quantity of water used for these purposes is unknown. Arsenal estimates of 200 gpm seem excessively large. At the request of The Ralph M. Parsons Company, meters are being installed on the water lines to the various buildings and separate facilities to determine the distribution of water within the plant. If these meters show excessive usage of water for equipment decontamination and washdown, a special system should be installed to recirculate the wash water. This procedure will necessitate the disposal of only a relatively small stream from this source.

These various streams are generally too small and too varied to recover and purify sufficiently for sale at a reasonable cost. It is recommended that these streams be dumped to the sealed reservoirs.

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THE USE OF INJECTION WELLS FOR DISPOSAL OF WASTES

The possibility of drilling a deep well and injecting the waste brines from the operations at the Arsenal was investigated. Dr. Thad McLaughlin, geologist and head of the Ground Water Branch of the United States Geological Survey in Denver, was consulted on this matter.

Dr. McLaughlin was strongly of the opinion that the technique of waste disposal by injection into a well, was not applicable in this case. In Dr. McLaughlin's opinion, an injection well would have to be drilled to the Dakota Sand formation to dispose of salt water without contamination of potable water supplies. In the Denver area the Dakota Sand is about 9 to 10 thousand feet below the surface. The cost of one well dug to this depth could be several hundred thousand dollars. The number of wells that might be needed to take the volume discharged by the various plants is a matter for wild guessing as it could be one or ten.

Injection wells can be an excellent and economical answer to disposal problems, when shallow, relatively inexpensive wells can be used. However, drilling injection wells is a gamble similar in risk to "wildcatting" for oil. Drilling deep injection wells is a very poor gamble as the costs are high and the potential winnings are small.

It is Dr. McLaughlin's opinion that injection wells should not be drilled. We concur with that opinion.

CONCLUSIONS AND RECOMMENDATIONS

1. The disposal of the chemical wastes from the various plants at Rocky Mountain Arsenal in a manner that will minimize the danger of contamination of underground water supplies, can be accomplished most economically by the following series of corrective measures and we strongly recommend their adoption:
 - a. Immediately reduce to a practical minimum the volume of contaminated water discharge by all plants.
 - b. Immediately install asphalt membrane seal in the existing 142 acres of reservoirs for an estimated cost of \$667,000. and use for temporary disposal of plant wastes. Plant No. 1 can be operated at only twenty per cent of capacity with this disposal facility.
 - c. Design and construct an acid purification plant for the by-products from Plant No. 1 for an estimated cost of \$2,050,000. Initiate a laboratory program for an estimated cost of \$5,000 to develop plant design data.
 - d. Design and construct facilities for neutralization of surplus acid, transferring resulting brine to existing evaporator plant, crystallize and stockpile salt. These facilities are to cost \$144,500.
 - e. Produce and sell as much pure acid as can be absorbed by the existing market. Neutralize any surplus acid and stockpile resulting salt.
 - f. Develop a process in the laboratory to purify the chlorides produced from Plant No. 2. This laboratory program can be initiated for four to five thousand dollars.
 - g. Dump all miscellaneous other wastes from the plants to the sealed reservoir system for solar evaporation.

Chlorine
Plant
conversion

This system will require an estimated total investment as summarized below:

Sealing Reservoirs	\$ 667,000
Purification Plant	2,050,000
Laboratory Programs (2)	10,000
Salt Stockpiling Facilities	<u>144,500</u>

TOTAL PROJECT COST \$2,871,500

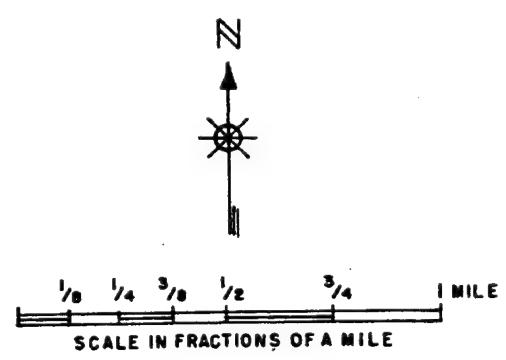
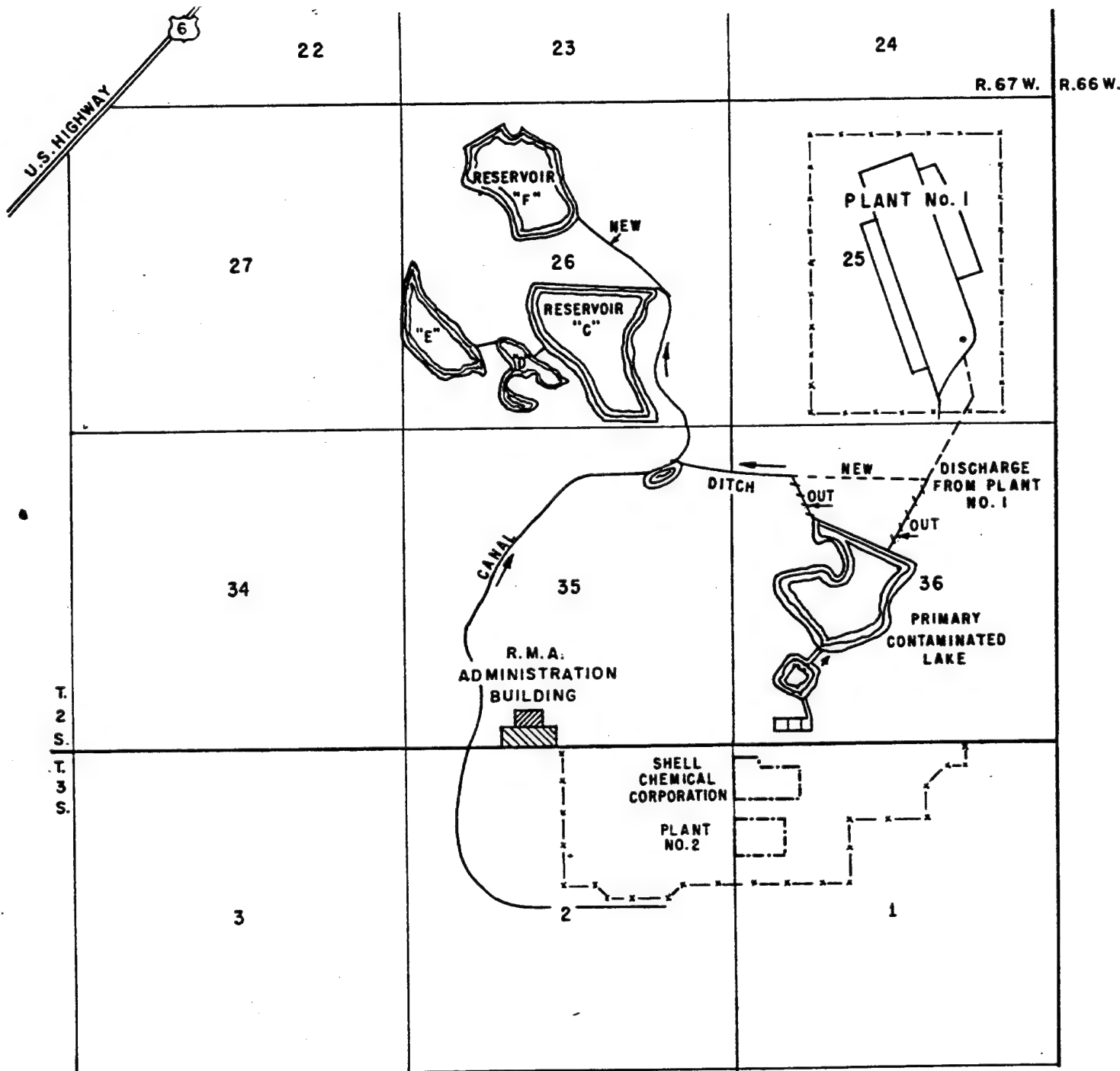
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It is estimated that this system will result in a reduced operating cost for disposal of the chlorides from Plant No. 1 below the cost of the present method and in addition will recover eight to nine thousand pounds of Plant No. 1 product per full operating day, which is now being lost using the present operating facilities and methods.

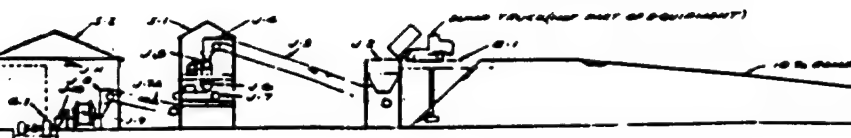
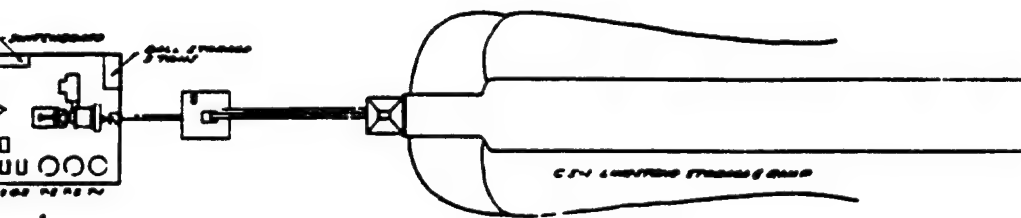
2. A detailed analysis of the cost data to be submitted this year by Hercules Powder Company on their catalytic chlorine process, should be made. If this data substantiates the estimates made by Hercules, the design and construction of a plant to convert hydrogen chloride from Plant No. 1 to chlorine by this process should be undertaken. A plant to perform this function is estimated by Hercules to cost \$1,350,000. Conversion of the by-product hydrogen chloride to chlorine has a wider and firmer market than does hydrochloric acid. The use of this catalytic chlorine process will give the lowest cost for disposal, if the estimate submitted by Hercules is correct.
3. Conversion of pure hydrogen chloride to chlorine via sodium chloride electrolysis in the existing plant is estimated to increase disposal cost considerably over the existing or other proposed disposal methods.

We would expect that conversion of the unpurified acid to chlorine by this method would be inoperable or considerably more expensive than conversion of the pure acid and would not permit recovery of the valuable products presently being lost.

4. The use of sealed reservoirs or injection wells to dispose of the wastes from all plants running at full capacity would be excessively costly, particularly if the by-product from Plant No. 1 is not purified of its phosphorus and fluoride contaminants.



THE RALPH M. PARSONS COMPANY LOS ANGELES	LAYOUT SKETCH OF ROCKY MOUNTAIN ARSENAL SHOWING PROPOSED SEALED RESERVOIR SYSTEM	DRAWING NO.	REV.
		1113-AD7	○



PLOT PLAN AND ELEVATION CALCIUM-PHOSPHATE FERTILIZER PLANT ROCKY MOUNTAIN ARSENAL DENVER, COLORADO THE RALPH M. HARRIS COMPANY AND ARCHT.		1113-AA1
--	--	----------

CS-1
LIMESTONE STORAGE
420 TONS - 14 DAYS

J-1
PAYLOADER
(FOR EMERGENCY ONLY)

R-1
BRIDGE

S
BIN
30 TONS / DAY

WINDOOST DUMP TRUCK

CS-1

J-2

J-3

J-4

J-5

J-6

J-7

J-8

WATER SUPPLY 3" DIA

FIRE LINE TO PLANT

NATURAL GAS SUPPLY 2 1/2" DIA

ACID SUPPLY (BY ARSENAL)

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J-2
BIN
30 T/DAY

J-3
BELT FEEDER
1.5 TPH @ 5 FPM
1 HP - YBFC
GEAR MOTOR
100 RPM

J-4
FEED CHUTE

J-5
HAMMER MILL
12" x 17" OPENING
15 HP HT MOTOR

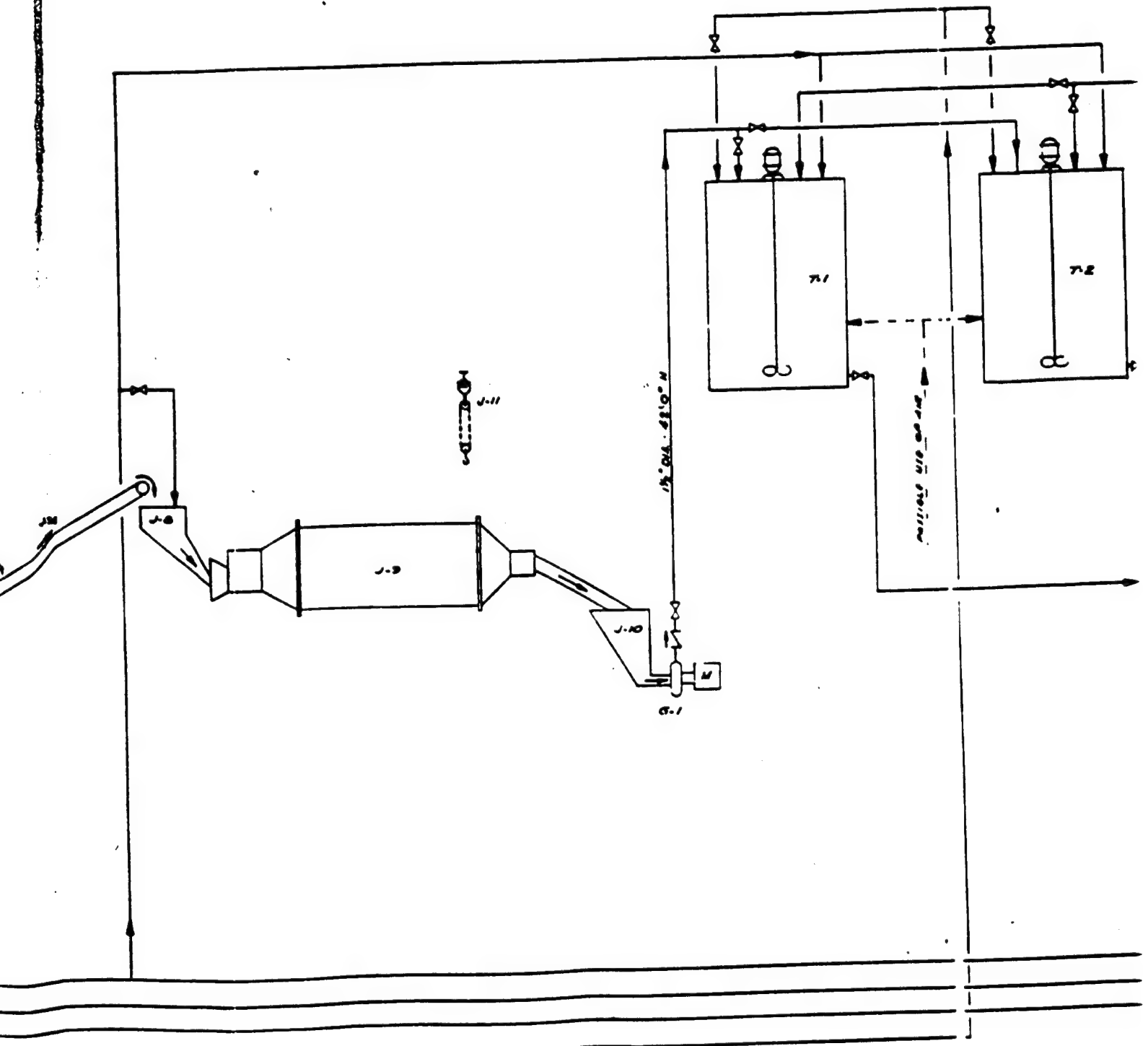
J-6
DISCHARGE BIN
1 TON CAPACITY

J-7
FEEDER
1.5 TPH - 1/2 HR

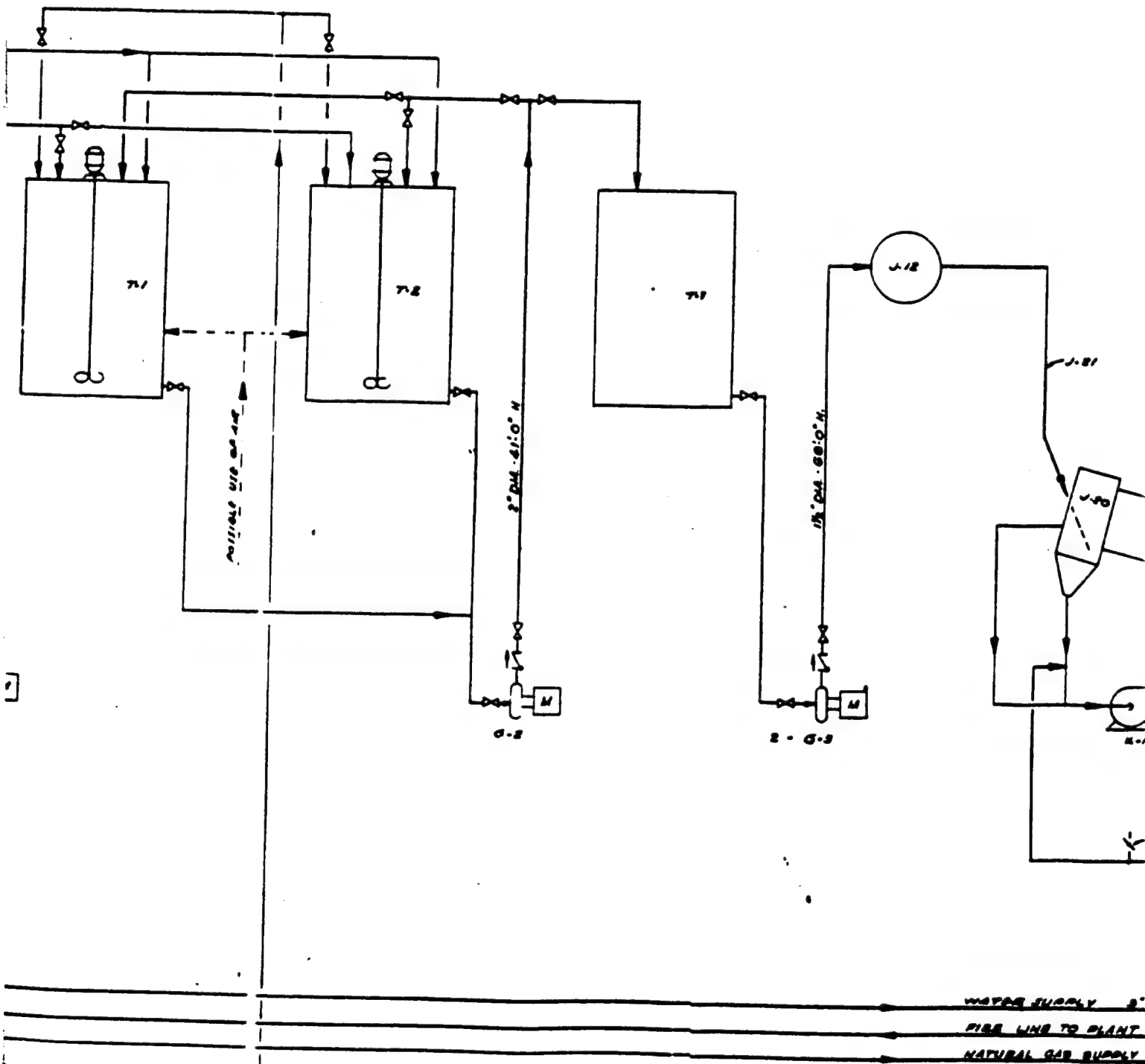
J-8
FEED CHUTE

J-9
BALL MILL DISC
25 HP - 900 RPM CH.
WOUND - ROTOR
MOTOR

J-7A
CONVEYOR
1/2 HP - 100 RPM
GEAR MOTOR



G-1
SLURRY PUMP



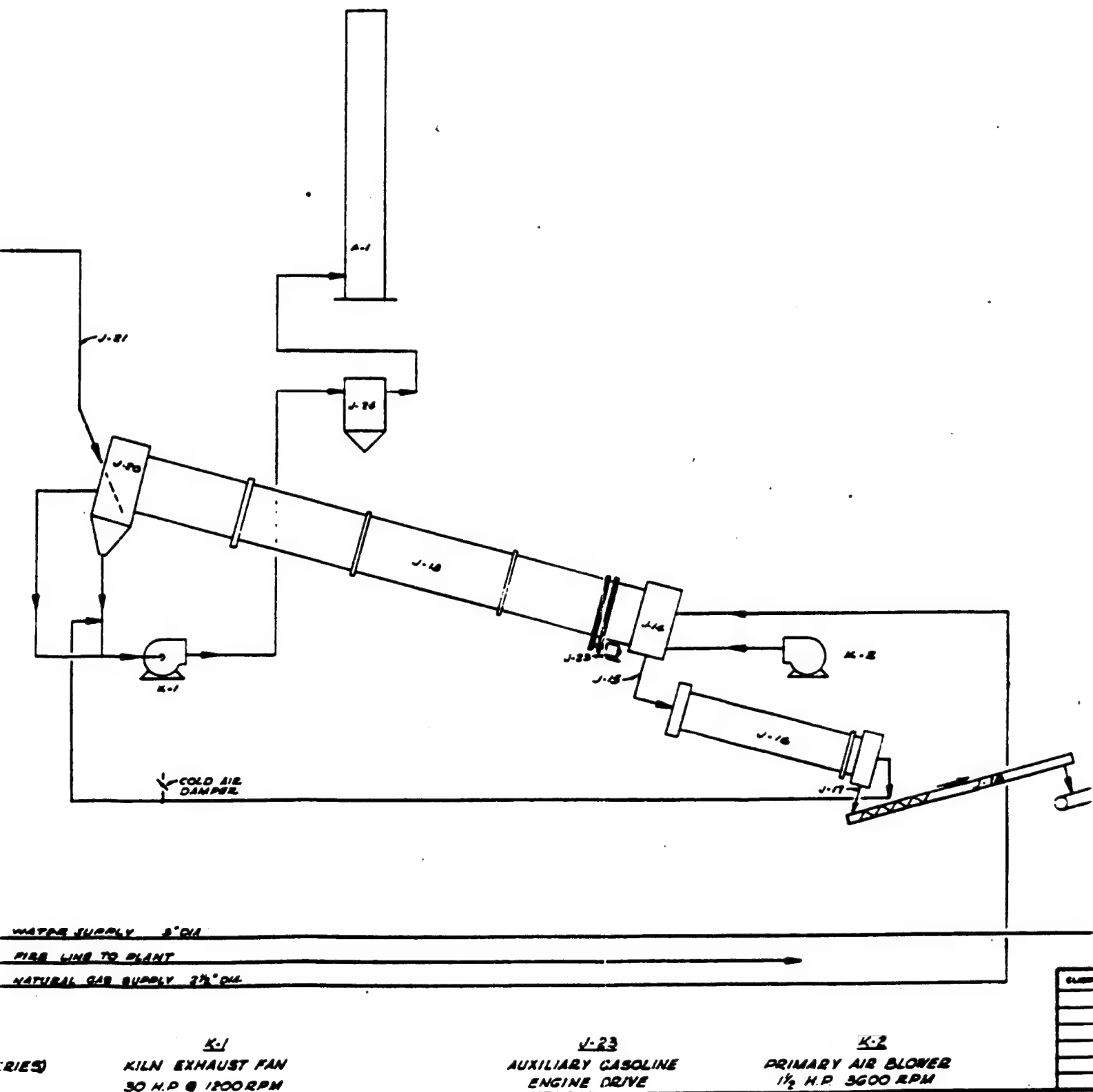
PUMP
1 GPM

G-2
CIRCULATING PUMP
3 HP - 30 GPM

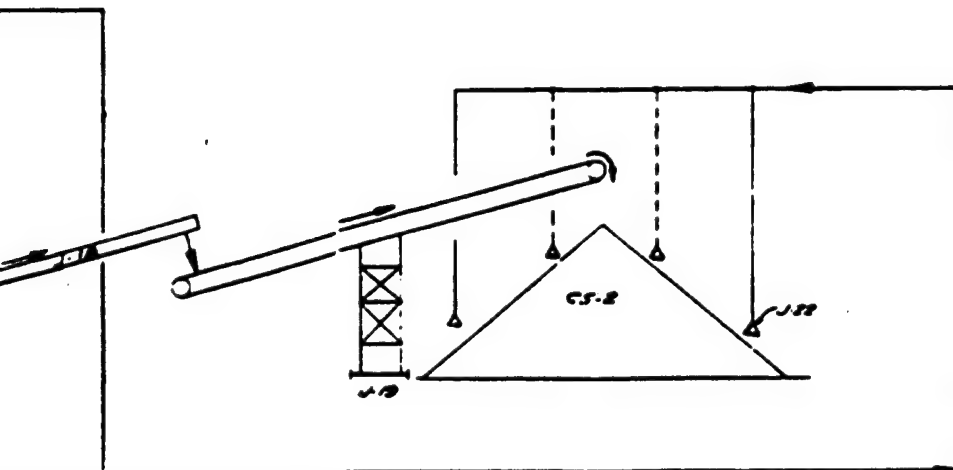
6-3
2-KILN FEED PUMPS (SERIES)
3HP-18 GPM

KILN E.
30 H.P.

J-24
MULTICLONE
DUST COLLECTOR



<u>J-15</u>	<u>J-16</u>	<u>J-17</u>	<u>J-18</u>	<u>J-19</u>	<u>J-22</u>	<u>CS-2</u>
DISCHARGE	COOLER	COOLER DISCHARGE	SCREW CONVEYOR	MOVABLE BELT	FOG NOZZLES	PRODUCT
CHUTE	3 HP - 1200 RPM	CHUTE	3/4 HP - 30 RPM GEAR MOTOR	STACKER 1 HP TEFC GEAR MOTOR 100 RPM		STOCKPILE



CLASH	APPL	NO	REV	REVISIONS	BY	CL	DATE	APPROVED	DATE	APPROVED
		0	1	DESIGNED FOR PROPOSAL	4.4	17	5-10-50	BY: J. C. L.		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		
								APPROVED FOR PROPOSAL		

PROCESS FLOW DIAGRAM
 CALCIUM-PHOSPHATE FERTILIZER PLANT
 ROCKY MOUNTAIN ARSENAL DENVER, COLORADO
 THE RALPH M. PARSONS COMPANY
 LOS ANGELES
 1113-AE2

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C-4004, C-4016

C-4027
STEP IX OFF-GAS
CONDENSER
(EXISTING)

E-2A, E-2B, E-2C

STEP IX DE GAS
CONDENSER
373 M BTU/HR
308 SQ.FT.
EACH UNIT

E-3A, E-3B, E-3C

STEP IX PRELIMINARY
CONDENSER
500 M BTU/HR
400 SQ.FT.
EACH UNIT

FROM STEP IX REACTOR



C-4004

80°F

70°F FC

FC RETURN

C0

FROM STEP IX REACTOR

104°F

600 MM HG

FROM DE GAS COLUMN

130°F

70 MM HG

EXPANSION VALVE

-40°F

40 MM HG

E-2

CONDENSATE RETURN

TO PROCESS

F-12 (LIQUID)

F-12 (GAS)

-50°F

FROM PRELIMINARY



130°F

70 MM HG

-40°F

40 MM HG

E-3

CONDENSATE RETURN

TO PROCESS

F-12 (LIQUID)

-50°F

F-12 (GAS)

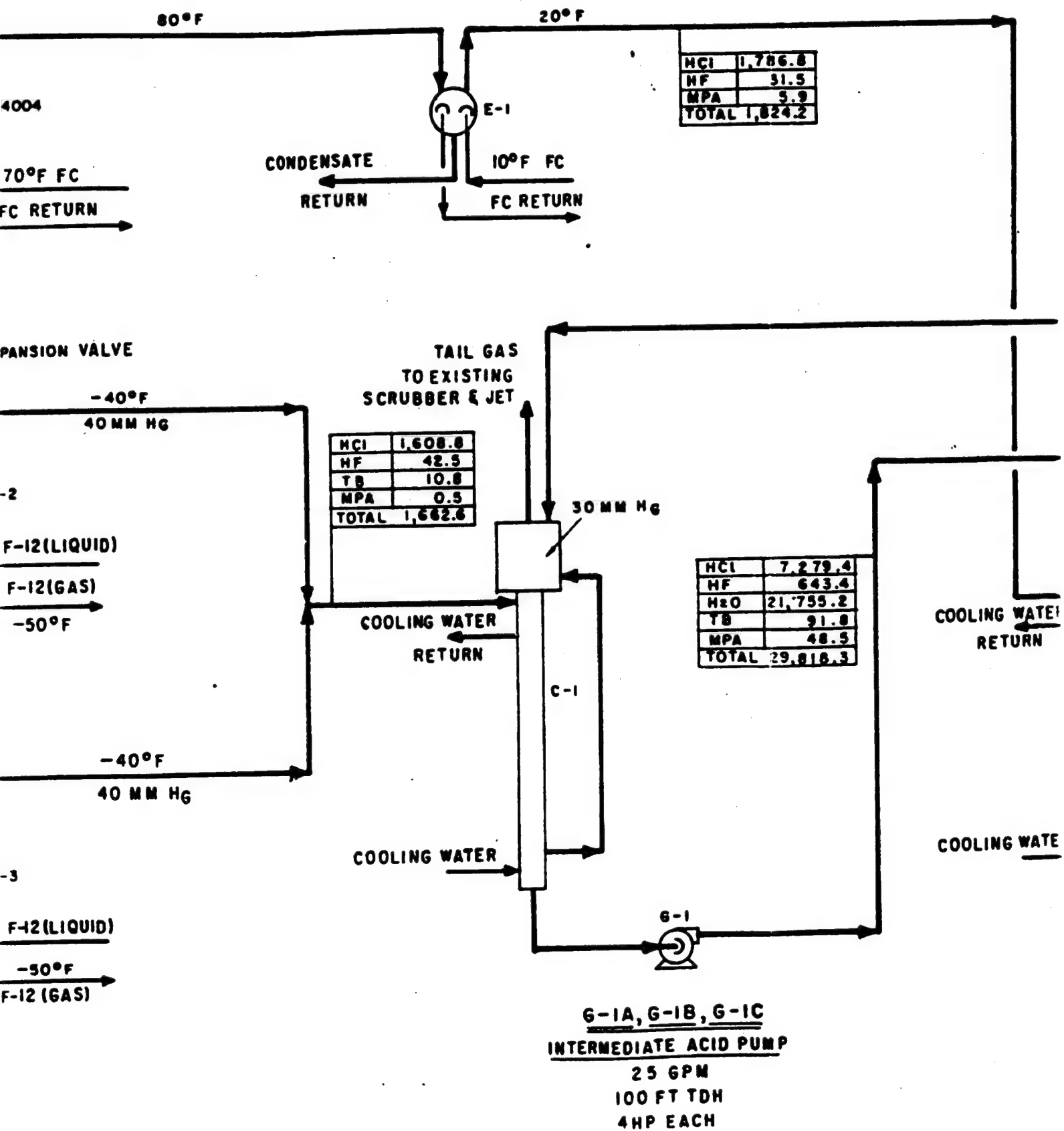
E-2C
AS
R
/HR
T.

E-3A, E-3B, E-3C
STEP X PRELIMINARY
CONDENSER
500 MBTU/HR
400 SQ. FT.
EACH UNIT

E-1A, E-1B, E-1C
OFF GAS CHILLER
36,000 BTU/HR
40 SQ. FT.
EACH UNIT

C-1A, C-1B, C-1C
STEP X, ACID
ABSORBER
350 MBTU /HR EACH

C-2A,
STE
AB
375 ME



C-2A, C-2B, C-2C
STEP IV ACID
ABSORBER
 375 MBTU/HR EACH

D-4
RECYCLE ACID
TANK
 300 GALLONS
 R.L. STEEL

CRI
 300
 R.

THREE
 IDENTICAL
 PROCESS
 LINES
 INSIDE
 BUILDING

ONE
 COMMON
 PROCESS
 LINE
 OUTSIDE
 BUILDING

HCl	9,066.2
HF	674.9
H ₂ O	21,755.2
TB	91.8
MPA	54.0
TOTAL	31,642.5

TAIL. GAS TO
 EXISTING
 SCRUBBER

650 MM Hg

COOLING WATER
 RETURN

C-2

COOLING WATER

G-2

G-2A, G-2B, G-2C
STRONG ACID PUMP
 25 GPM EACH
 30 FT TDH
 1 HP EACH

G-9

G-9
RECYCLE ACID PUMP
 70 GPM
 40 FT TDH
 3 HP

VENT

D-4.

8
 5
 9
 2

279.4
 643.4
 755.2
 91.8
 48.5
 818.3

D-4
RECYCLE ACID
TANK
300 GALLONS
R.L. STEEL

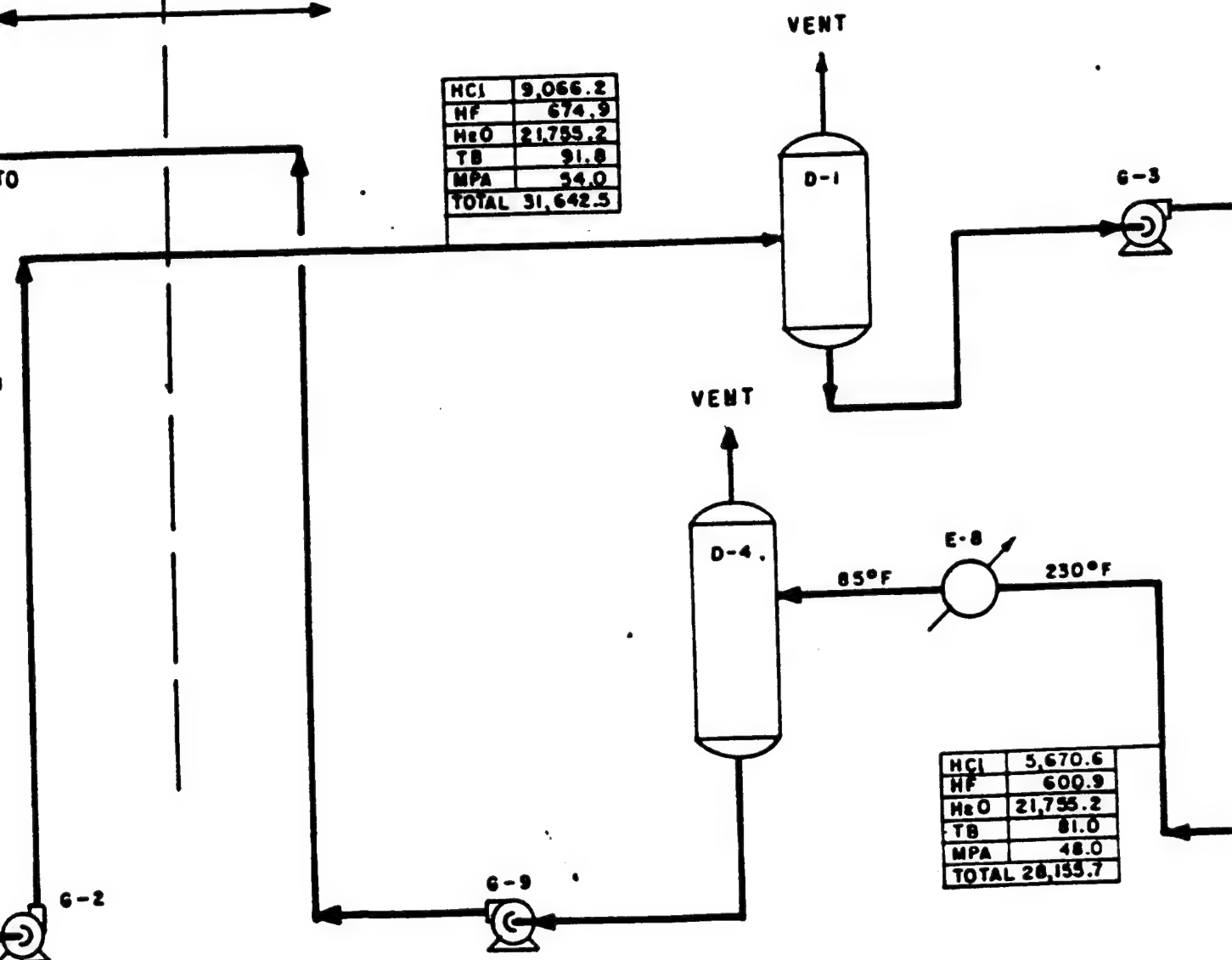
D-1
CRUDE ACID
TANK
300 GALLONS
R.L. STEEL

E-8
RECYCLE ACID
COOLER
4.1 MM BTU/HR
855 SQ. FT.
HASTELLOY B

THREE
IDENTICAL
PROCESS
LINES
INSIDE
BUILDING

ONE
COMMON
PROCESS
LINE
OUTSIDE
BUILDING

HCl	9,066.2
HF	674.9
H ₂ O	21,755.2
TB	91.8
MPA	54.0
TOTAL	31,642.5



G-2B, G-2C
6 ACID PUMP
6 GPM EACH
0 FT TDH
1 HP EACH

G-9
RECYCLE ACID PUMP
70 GPM
40 FT TDH
3 HP

G-3
PRIMARY COLUMN
FEED PUMP
80 GPM
50 FT TDH
1 HP

G-
PRIMAR
REFL
4 G

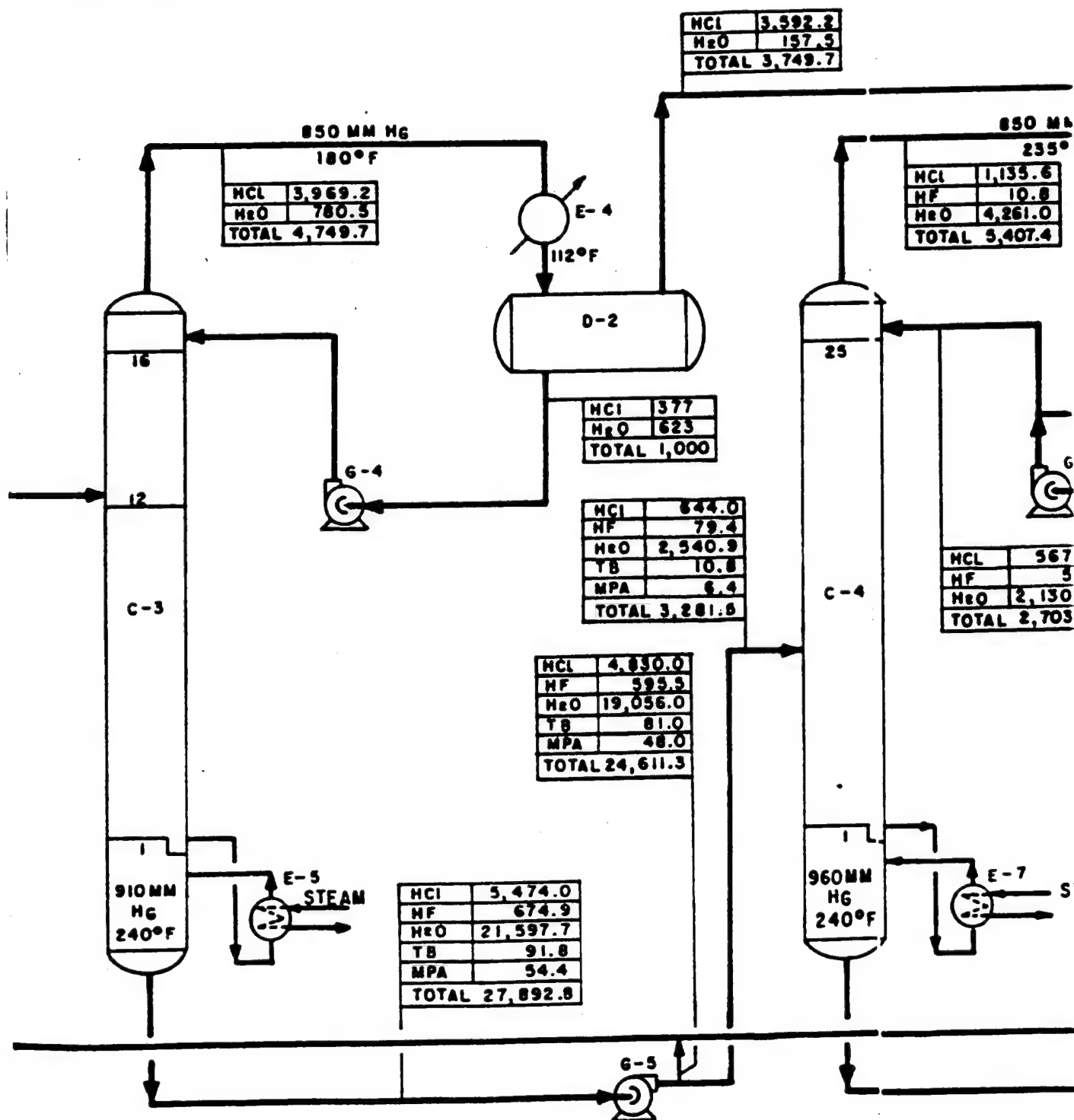
C - 3
PRIMARY ACID
COLUMN
3'-0" x 30'-0"
16 TRAYS
HASTELLOY B

D - 2
PRIMARY COLUMN
REFLUX DRUM
50 GALLONS
HASTELLOY B

E - 4
PRIMARY COLUMN
CONDENSER
1.2 MM BTU/HR.
535 SQ. FT.
HASTELLOY B

C - 4
SECONDARY
ACID COLUMN
3'-0" x 15'-0"
25 TRAYS
HASTELLOY B

E - 6
SECONDARY
CONDENSER
5.1 MM BTU/HR.
734 SQ. FT.
HASTELLOY B



-4
RY COLUMN
UX PUMP
GPM

E - 5
PRIMARY COLUMN
REBOILER
6.6 MM BTU/HR
590 SQ. FT.
HASTELLOY B

G - 5
SECONDARY COLUMN
FEED PUMP
80 GPM
50 FT TDH
3 HP

E - 7
SECONDARY COLUMN
REBOILER
5.1 MM BTU/HR
HASTELLOY B

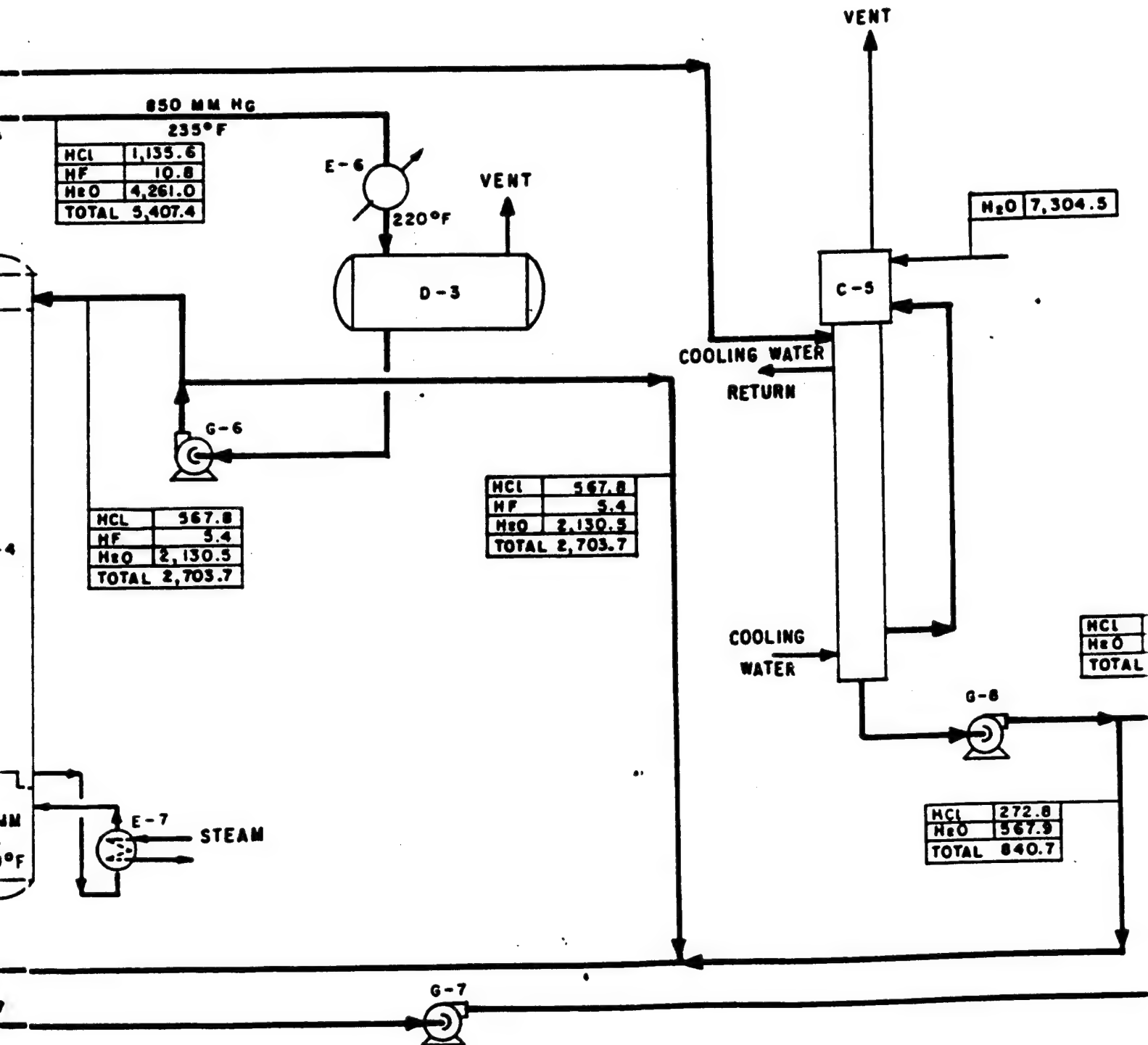
SECONI
REFL
15
50

4
SECONDARY COLUMN
 15'-0"
 HASTELLOY B

E-6
SECONDARY COLUMN
CONDENSER
 5.1 MM BTU/HR
 734 SQ. FT.
 HASTELLOY B

D-3
SECONDARY COLUMN
REFLUX DRUM
 300 GALLONS
 HASTELLOY B

C-5
PURE ACID
ABSORBER
 1,954 M BTU/HR.



G-6
SECONDARY COLUMN
REFLUX PUMP
 15 GPM
 50 FT TDH
 2 HP

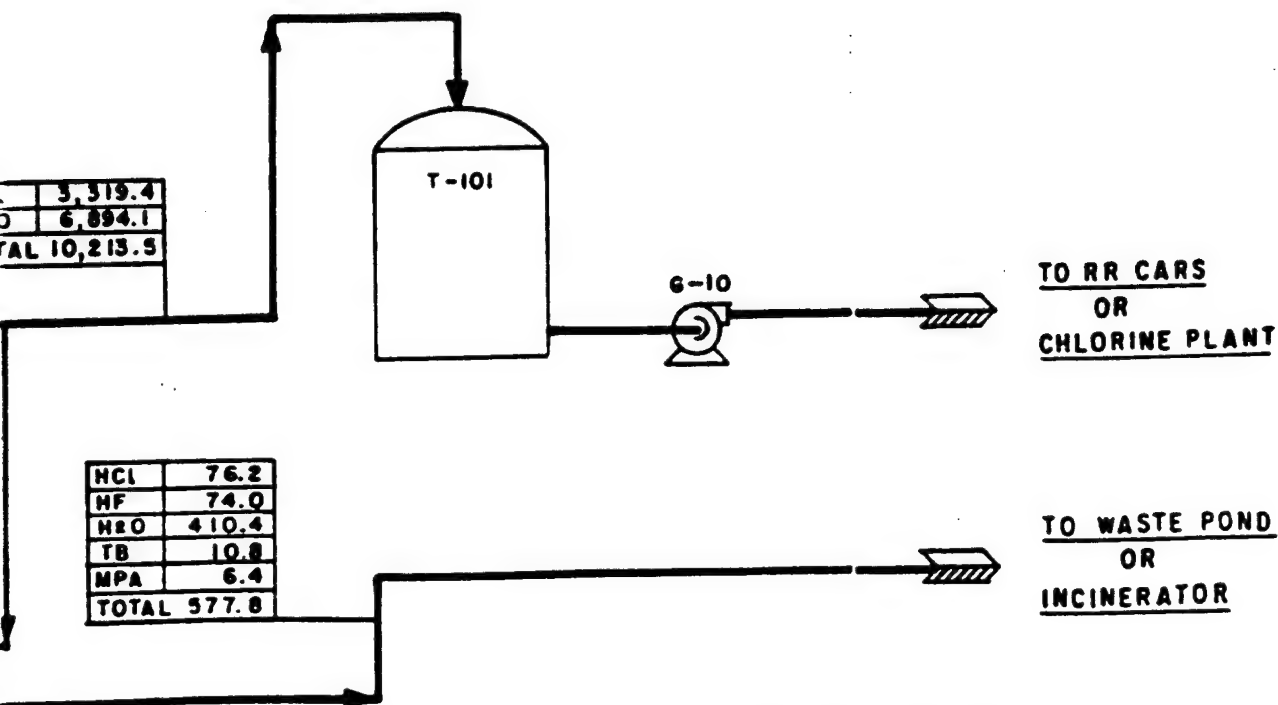
G-7
SECONDARY COLUMN
BOTTOMS PUMP
 2 GPM
 100 FT TDH
 10 HP

G-8
PURE ACID
PUMP
 25 GPM
 100 FT TDH
 10 HP

G-10
PURE ACID
TRANSFER PUMP
 100 GPM
 50 FT TDH
 5 HP

T-101A, T-101B
PURE ACID
STORAGE TANKS
 50,000 GALLONS EACH
 R.L. STEEL

1. MATERIAL FLOW QUANTITIES IN
2. THE FOLLOWING SYMBOLS ARE USED
 - FC - CH₂CL₂ LIQU
 - F-12 - FREON-12
 - TB - ISOPROPYL AL
 - MPA - METHYL PHO



CLIENT APPROVAL	NO	DATE	REVISION	APPROVED		DESIGN	
				PROCESS ENGR.	CH. PROC ENGR.	DRAWN	STAN PRUSS
	0		ISSUED FOR STUDY				CRD.
							APP. CH. DRAFT.
							APP. CH. PROC. ENGR.
							APP. PROJECT ENGR. <i>[Signature]</i>
							APP. CH. ENGR.
							DATE

PROCESS FLOW

ACID PURIFICATION

ROCKY MOUNTAIN

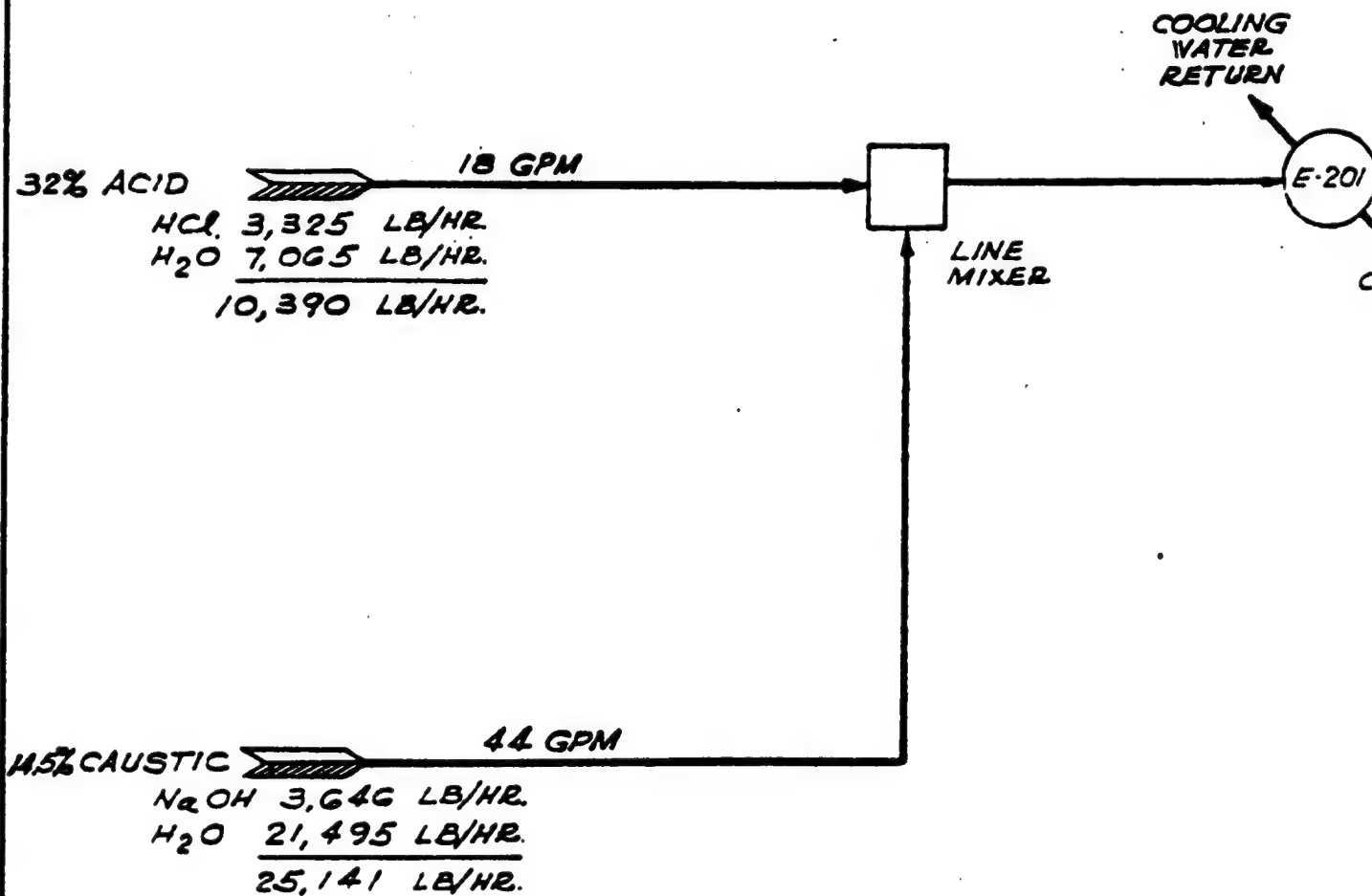
THE RALPH M. PARSONS
COMPANY
LOS ANGELES

BY

111

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E-201
BRINE CO
250 SQ.FT. T/C
MONEL T/C



E-201

IS COOLER

FT. 1,000 MBTU/HR.

NEL TUBES

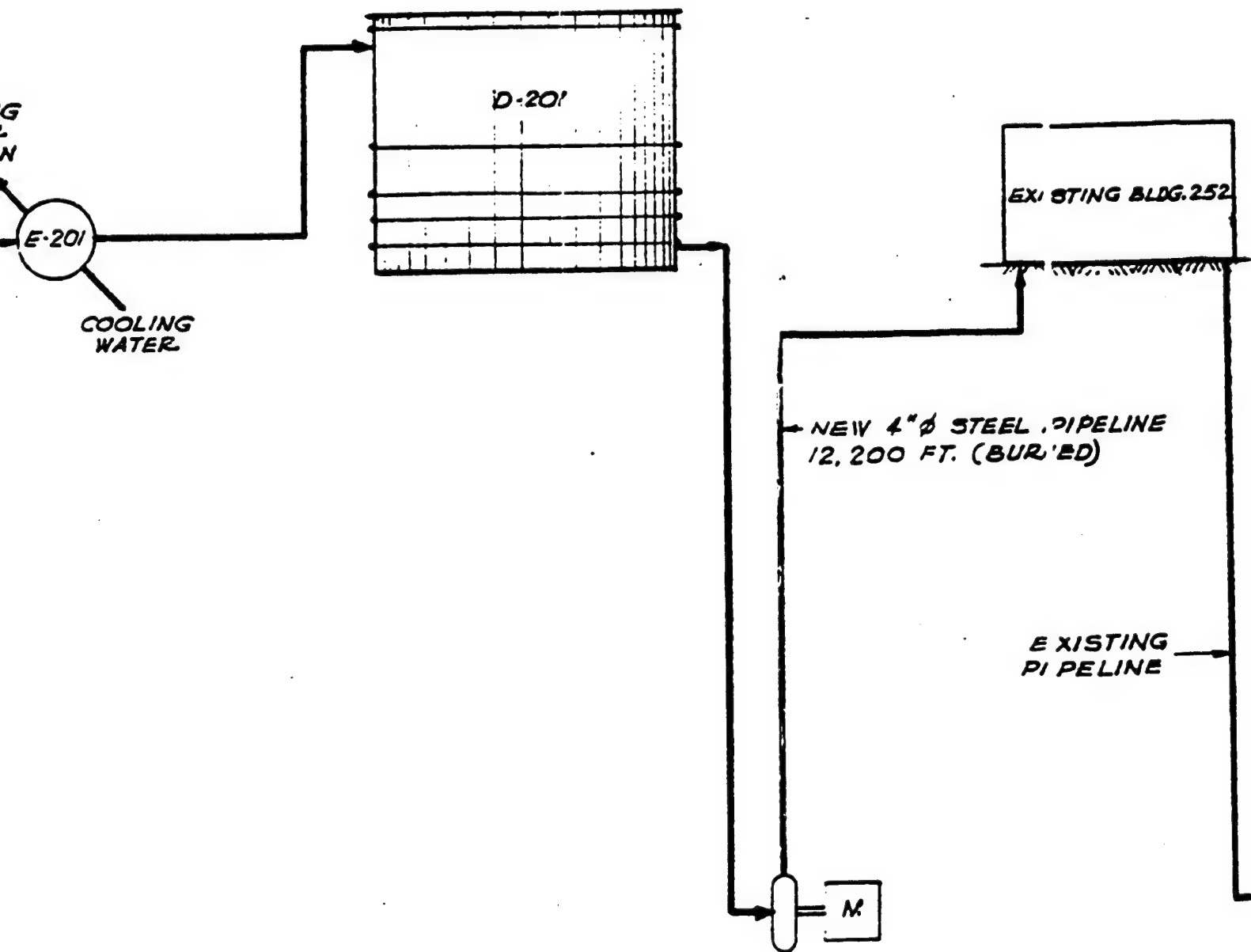
D-201

BRINE SURGE TANK

10,000 GAL. - VERTICAL

12'-0" DIA. x 12'-0"

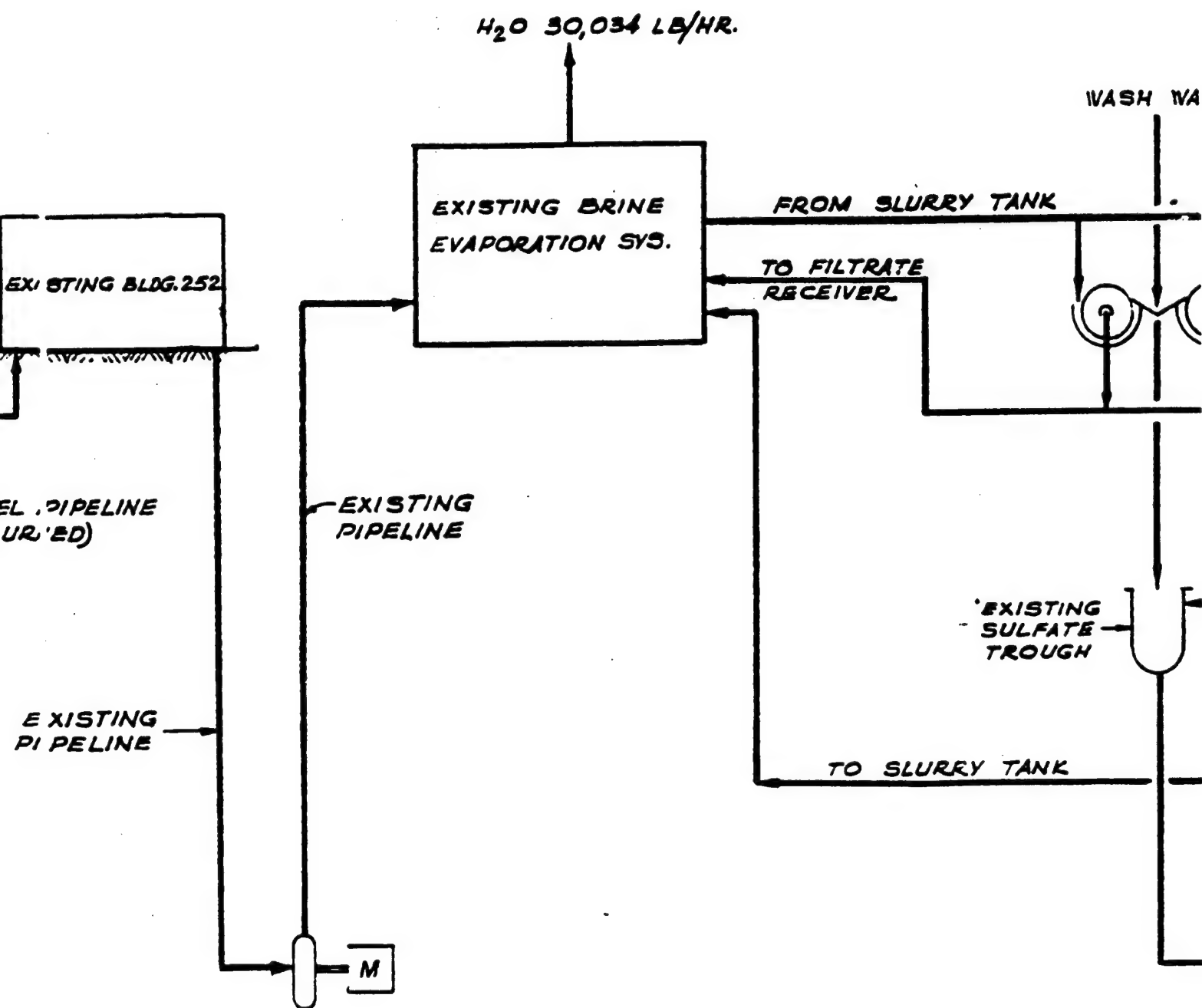
REDWOOD TANK



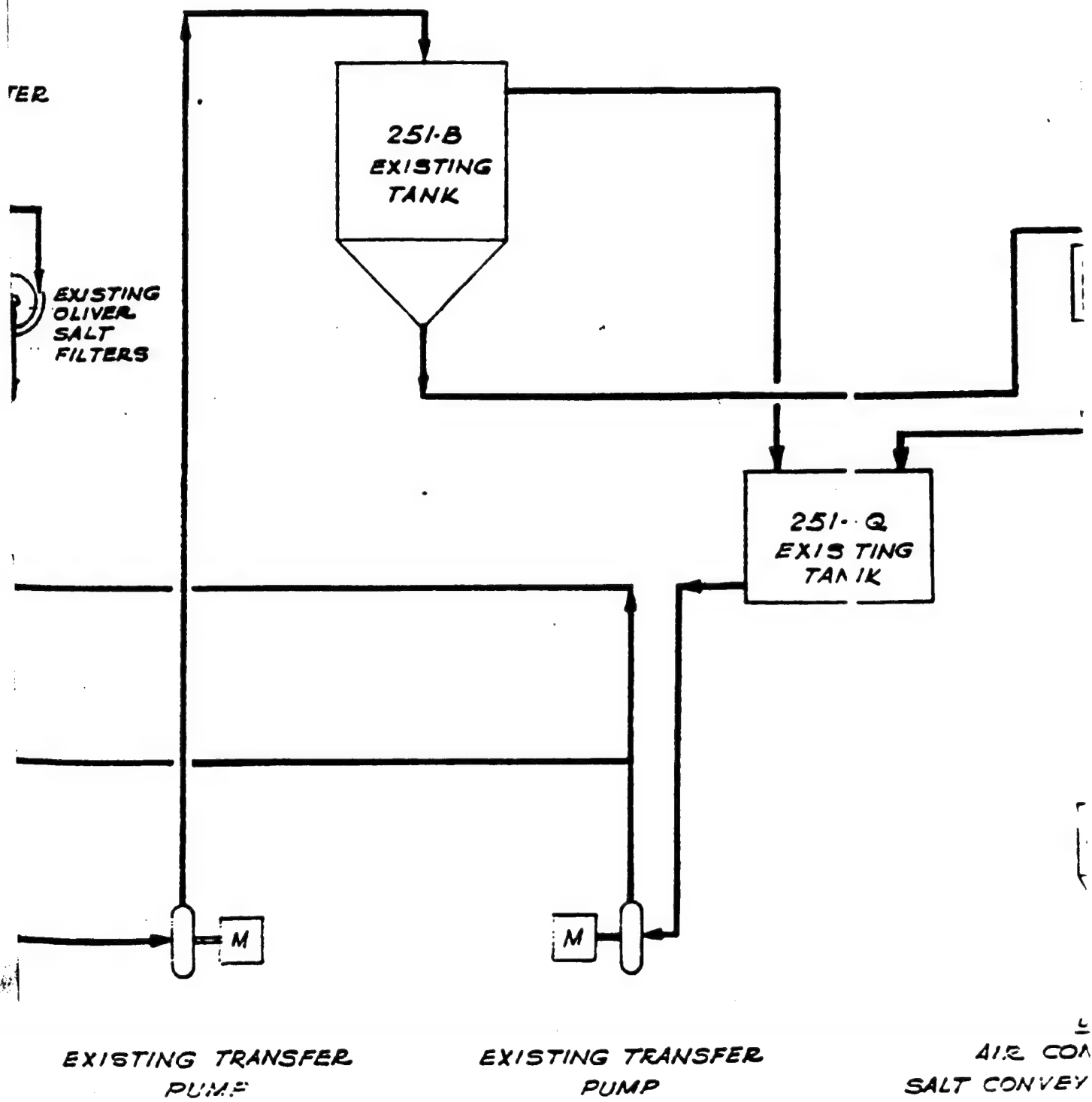
G-201 & SPARE

BRINE FORWARDING PUM. D

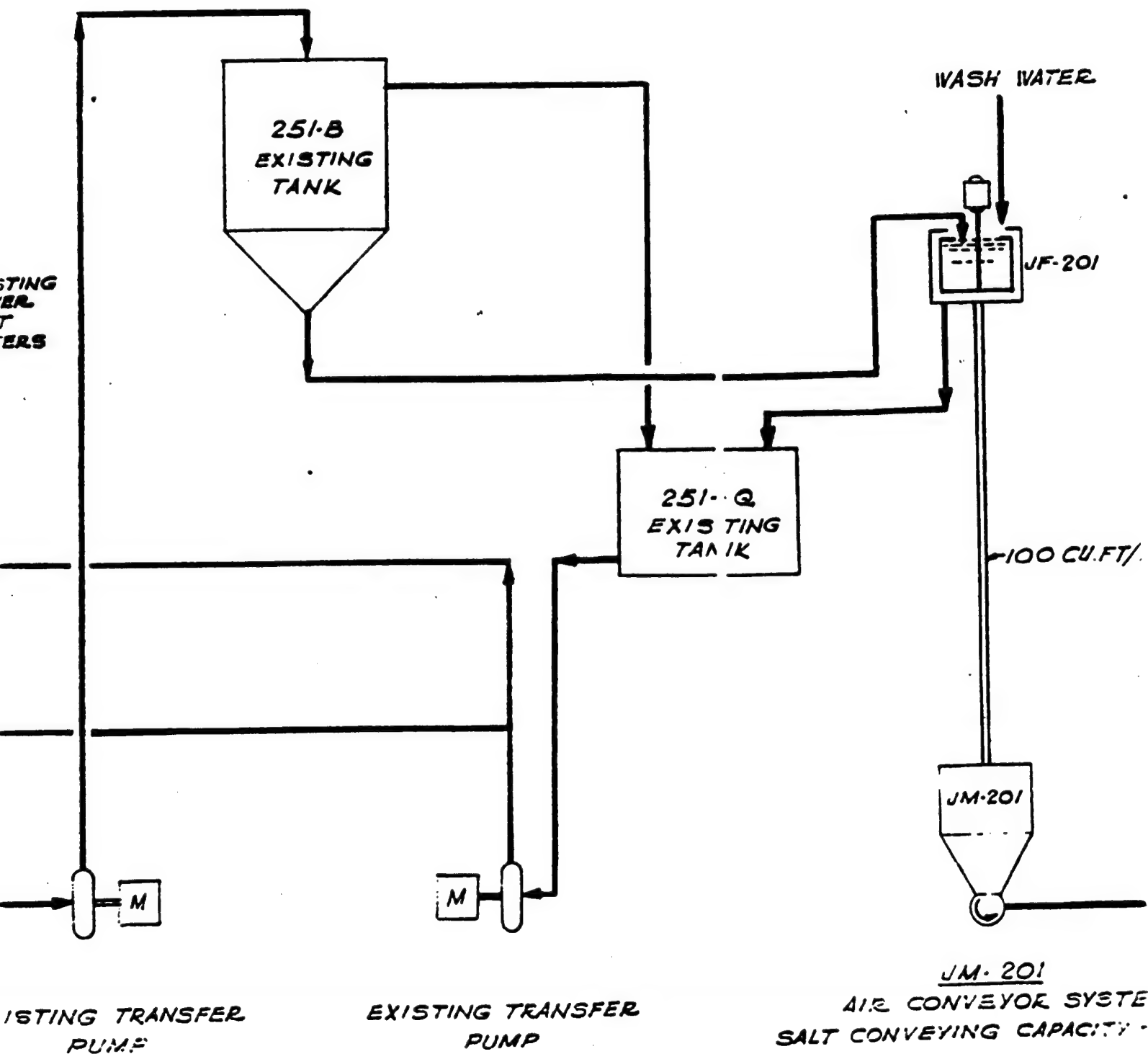
3 H.P. 64 GPM

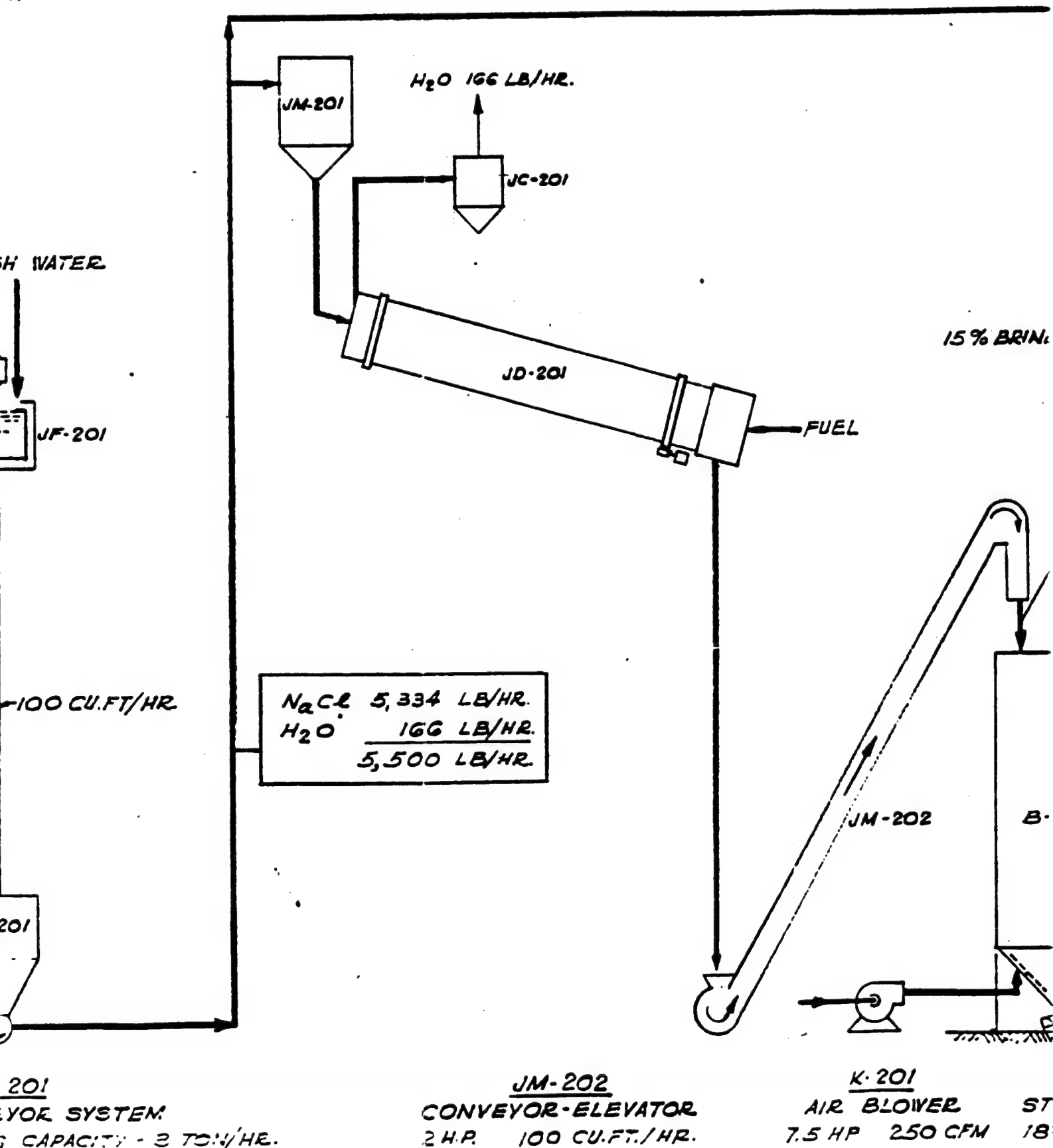


AL
B
CE



JF-201
AUTOMATIC
BATCHING
CENTRIFUGAL
30 HP





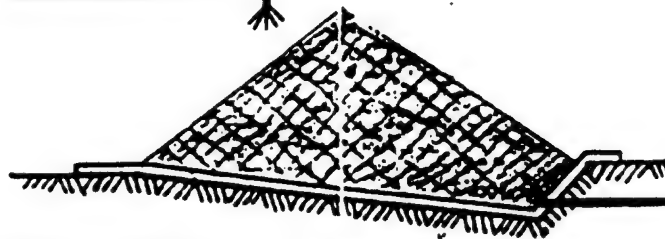
B-201
SALT DRYER
TON/HR., 3% H₂O

B-202
OUTSIDE STORAGE SLAB
150'x470'

G-202
BRINE TRANSFER
5 H.P. 150'

TO
EVAPORATORS

15% BRINE 145 GPM



G-202

FUEL

NaCl 5,334 LB/HR.
100 CU.FT./HR.

B-202

JM-202

B-201

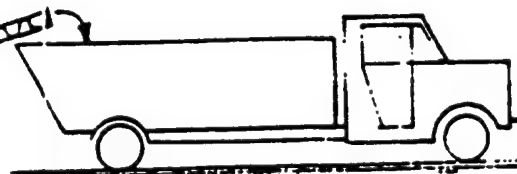


K-201
AIR BLOWER
5 HP 250 CFM

B-201
STORAGE SILO
18'-0" DIA. x 50'-0"

JM-203

JM-203
CONVEYOR-ELEVATOR
10 H.P. 1,000 CU.FT./HR.

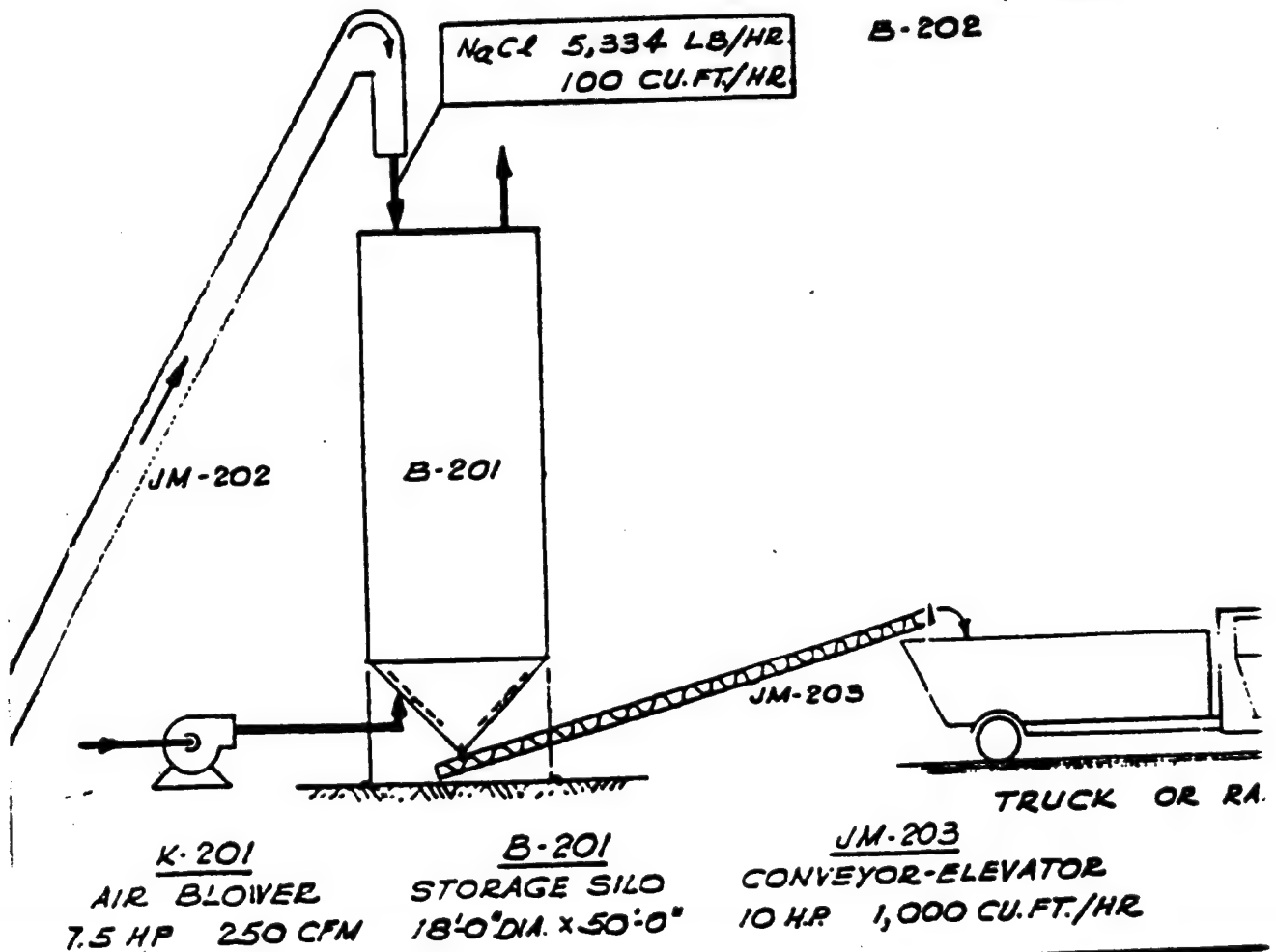
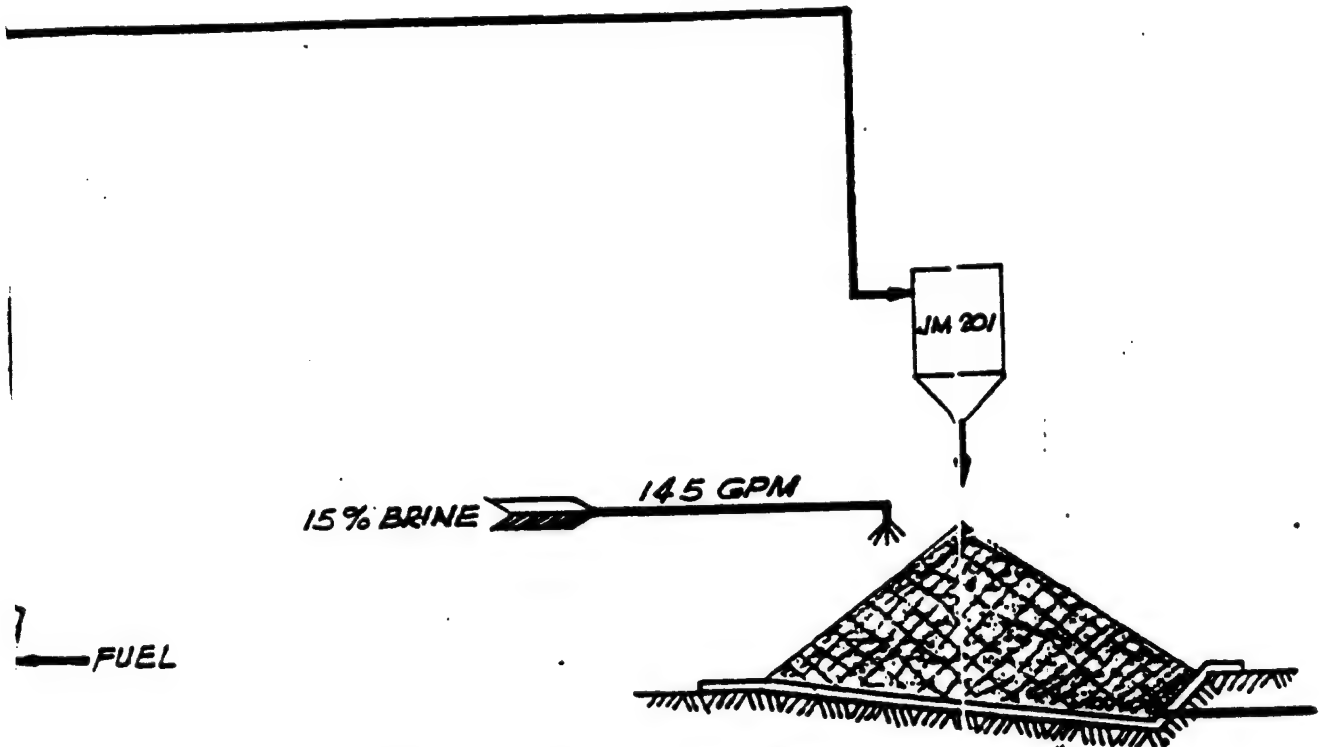


TRUCK OR RAIL CAR



JD-201
RY SALT DRYER
2.5 TON/HR., 3% H₂O

B-202
OUTSIDE STORAGE SLAB
150'x475'
TO
EVAPORATORS



B-201
SALT DRYER
TON/HR., 3% H₂O

B-202
OUTSIDE STORAGE: SLAB
150'x470'

G-202
BRINE TRANSFER P
5 H.P. 150 gpm

TO
EVAPORATORS

15% BRINE 145 GPM

FUEL

G-202

B-202

N₂Cl 5,334 LB/HR
100 CU.FT/HR

JM-202

B-201

JM-203

TRUCK OR RAIL CAR

K-201
AIR BLOWER
5 HP 250 CFM

B-201
STORAGE SILO
18'-0" DIA. x 50'-0"

JM-203
CONVEYOR-ELEVATOR
10 H.P. 1,000 CU.FT./HR

CLK
APPR

-202

TRANSFER PUMP
150 gpm

1

2

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	6	9/9/5	ISSUED FOR APPROVAL			CHK.
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						APP. CH. PROC. ENGR.
						APP. PROJECT ENGR. <i>RD</i>
						APP. CH. ENGR.
						DATE 9-8-55

PROCESS FLOW DIAGRAM	
DISPOSAL OF HYDROGEN CYANIDE BY METHOD "C"	
ROCKY MOUNTAIN ARSENAL DENVER, CO.	
THE RALPH M. PARSONS COMPANY LOS ANGELES	DRAWING 1113-A

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0	9/9/55	ISSUED FOR APPROVAL			CHKD.
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					APP. CH. PROC. ENGR.
					APP. PROJECT ENGR. <i>[Signature]</i>
					APP. CH. ENGR.
					DATE 9-9-55

PROCESS FLOW DIAGRAM

DISPOSAL OF HYDROGEN CHLORIDE

METHOD "C"

ROCKY MOUNTAIN ARSENAL DENVER, COLO.

THE RALPH M. PARSONS
COMPANY
LOS ANGELES

DRAWING NO.

1113-AE5

REV.

○

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B-101
NEW COLLECTING SUMP
6'-0" x 8'-0" x 7'-0" DEEP
ACID-BRICK LINING

	T/M
NaOH	935
H ₂ O	935
	<u>1,870</u>

50% CAUSTIC



9

PROCI

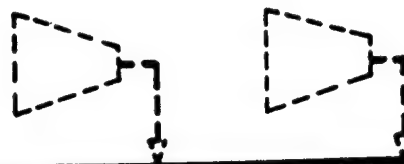
MISCELLANEOUS SOURCES

CAKE FROM PRESSURE FILTERS; SCRUBBER O
 NASH VACUUM PUMP OVERFLOW; AIR WASHER

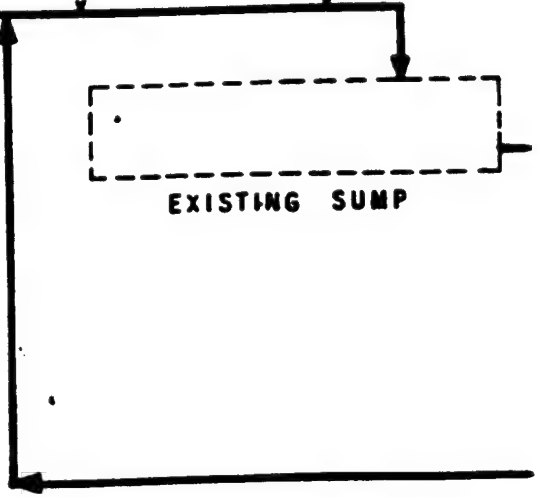


EXISTING BIRD CENTRIFUGAL

STEAM
 (OPTIONAL)



EXISTING SUMP

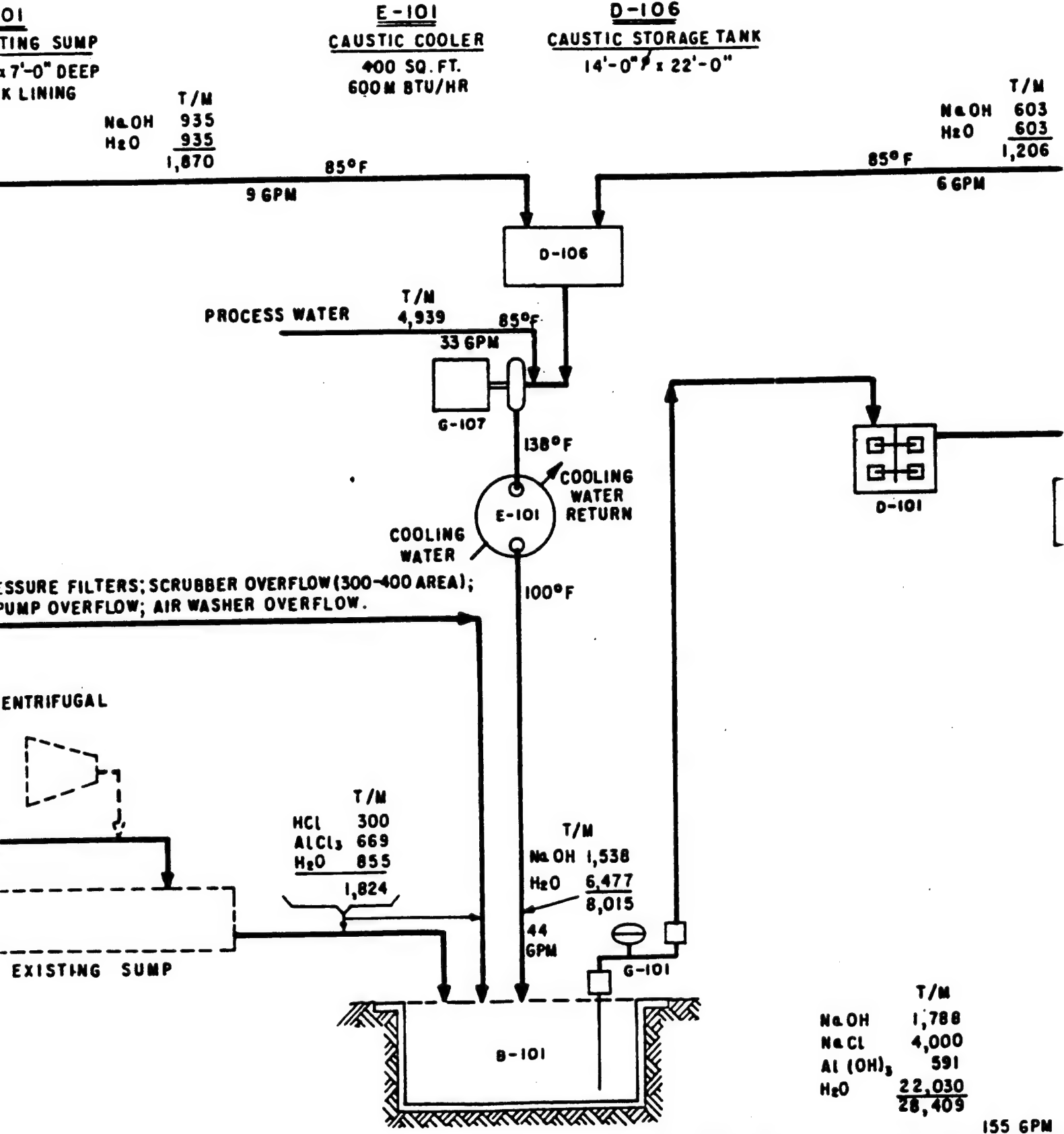


G-107 & SPA

CAUSTIC FEE

1 HP 4¢

EAC



G-107 & SPARE G-107A
CAUSTIC FEED PUMPS
1 HP 44 GPM
EACH

G-101
SUMP PUMP
100 CFM AIR @ 30 PSIG
40 CFM VACUUM @ 15 IN. Hg

BRIN
51

AGE TANK
2'-0"

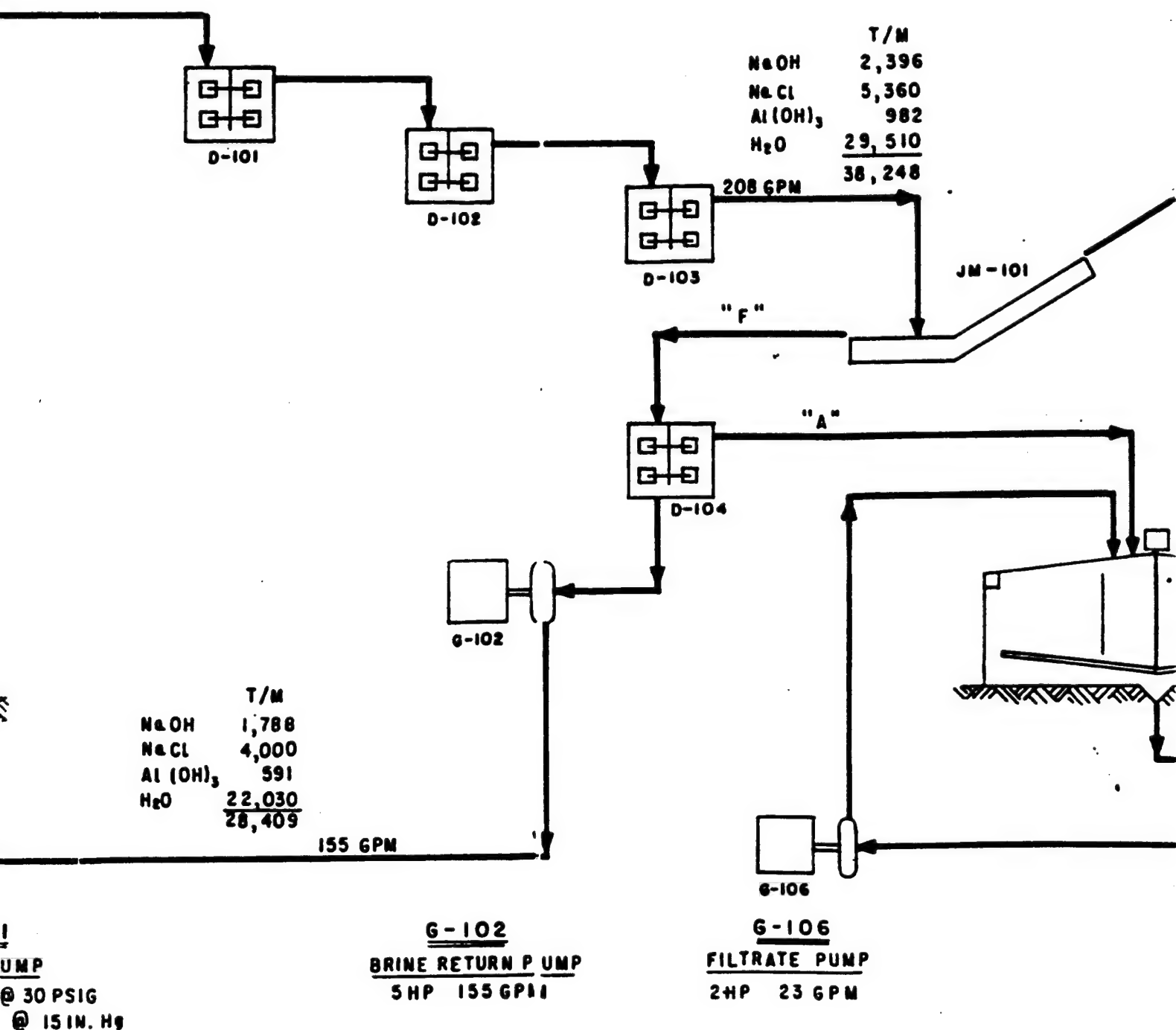
D-101, D-102, D-103
3- PADDLE - AGITATED TANKS
14'-0" DIAM. x 14'-0"
2 HP EACH

D-104
BRINE SURGE TANK
14'-0" x 14'-0"
2 HP

JM-101
RAKE CLASSIFIER
4'-0" x 15'-0"
2 HP

85° F
NaOH 603
H₂O 603
1,206
6 GPM

50% CAUSTIC RETURNED
FROM EVAPORATORS.



D-102, D-103
AGITATED TANKS
 DIAM. x 14'-0"
 P EACH

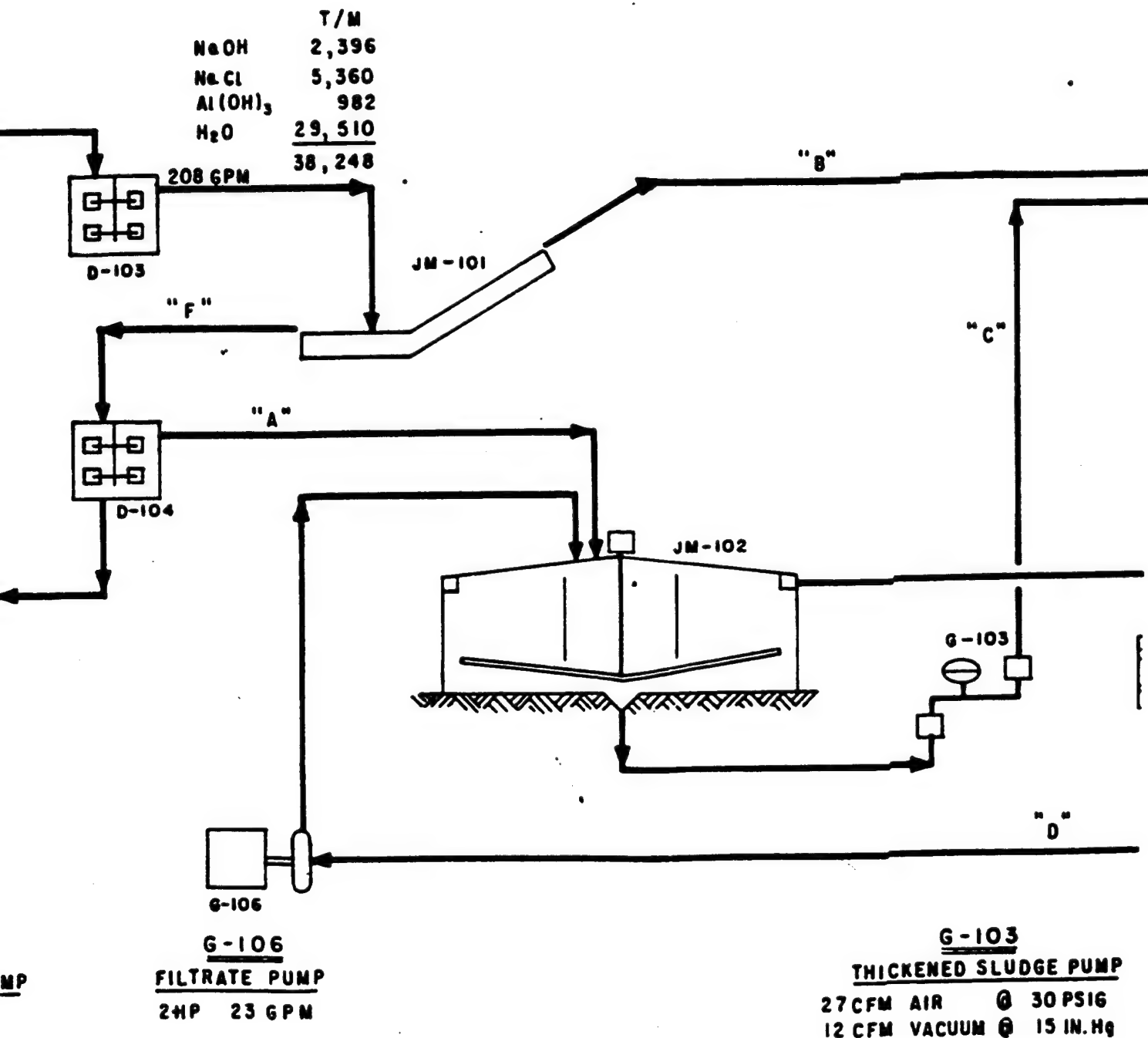
D-104
BRINE SURGE TANK
 14'-0" x 14'-0"
 2 HP

JM-101
RAKE CLASSIFIER
 4'-0" x 15'-0"
 2 HP

JM-102
CLARIFLOCCULATOR
 30'-0" x 9'-0"
 2 HP

JF-101
2 - SA
 12'-

50% CAUSTIC RETURNED
 FROM EVAPORATORS.



D-104
WINE SURGE TANK
 14'-0" x 14'-0"
 2 HP

JM-101
RAKE CLASSIFIER
 4'-0" x 15'-0"
 2 HP

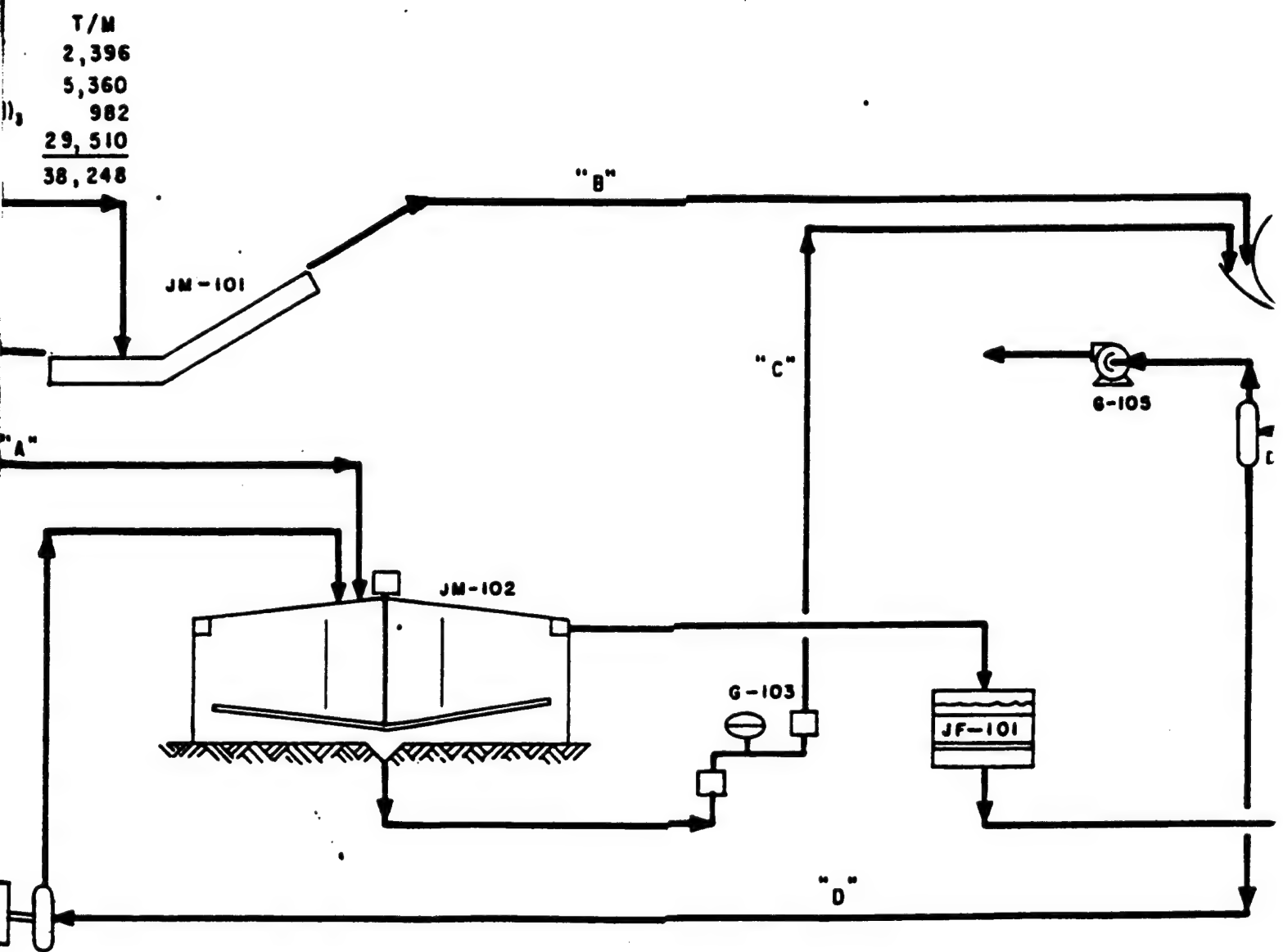
JM-102
CLARIFLOCCULATOR
 30'-0" x 9'-0"
 2 HP

JF-101A, JF-101B
2 - SAND FILTERS
 12'-0" x 10'-0"

J
ROTARY
 5'

AUSTIC RETURNED
APORATORS.

PROC



D6
PUMP
 6 GPM

G-103
THICKENED SLUDGE PUMP
 27 CFM AIR @ 30 PSIG
 12 CFM VACUUM @ 15 IN.Hg

G-105
VACUUM PUMP
 20 HP 250 CFM

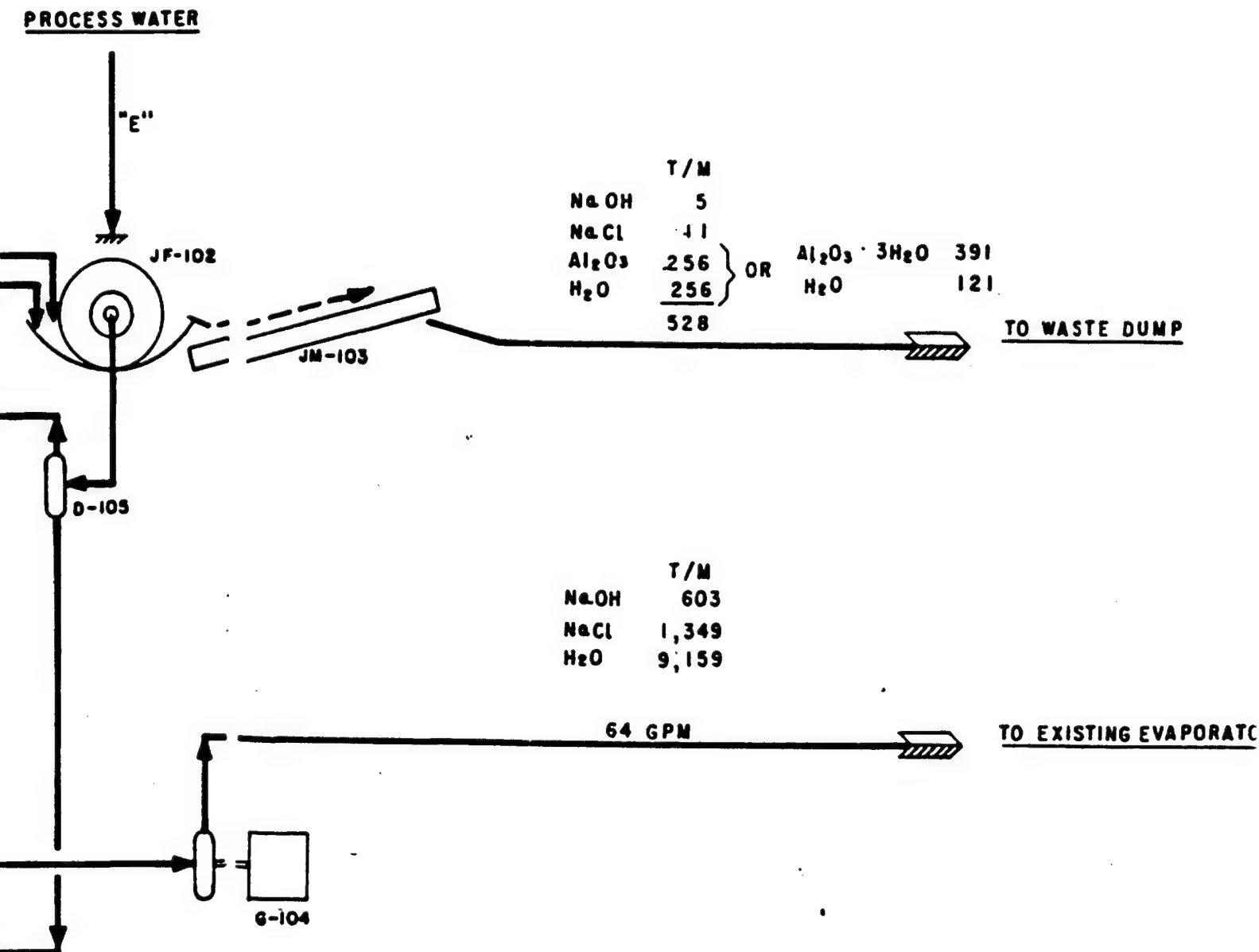
JF-102
ROTARY DRUM FILTER
 5'-3" x 5'-0"

JM-103
ALUMINA CAKE CONVEYOR

D-105
FILTRATE RECEIVER
 24" DIAM. x 48"

T

	A	B
NaOH	588	20
NaCl	1,316	44
Al ₂ O ₃ · 3H ₂ O	195	196
H ₂ O	<u>7,240</u>	<u>240</u>
TOTAL	9,339	500
GPM	51	3



UMP
 CFM

G-104
CLEAR BRINE
TRANSFER PUMP
 11HP 64 GPM

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						APP. CH. PROC. ENGR.
						APP. PROJECT ENGR.
						APP. CH. ENGR.
						DATE

D-105
FILTRATE RECEIVER

24" DIAM. x 48"

	TONS / MONTH					
	A	B	C	D	E	F
NaOH	588	20	101	116	—	2,376
NaCl	1,316	44	227	260	—	5,316
Al ₂ O ₃ · 3H ₂ O	195	196	195	—	—	786
H ₂ O	<u>7,240</u>	<u>240</u>	<u>1,542</u>	<u>3,461</u>	<u>1,800</u>	<u>29,270</u>
TOTAL	9,339	500	2,065	3,837		37,748
GPM	51	3	12	23	12	205

T/M

5

41

256

256

528

OR

Al₂O₃ · 3H₂O 391

H₂O 121

TO WASTE DUMP

T/M

603

1,349

9,159

TO EXISTING EVAPORATORS

NO.	DATE	REVISION	APPROVED		DESIGN
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0		ISSUED FOR STUDY			CD.
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					APP. CH. PROC. ENGR.
					APP. PROJECT ENGR.
					APP. CH. ENGR.
					DATE

PROCESS FLOW DIAGRAM CHLORIDE RECOVERY SYSTEM FOR PLANT NO. 2 ROCKY MOUNTAIN ARSENAL		
THE RALPH M. PARSONS COMPANY LOS ANGELES	DRAWING NO. 1113-AC6	REV. C

SUPPLEMENT TO THE FINAL REPORT

PCM-1606
RGM:jm
10-24-55

SUPPLEMENT TO THE FINAL REPORT

DISPOSAL OF CHEMICAL WASTES

ROCKY MOUNTAIN ARSENAL

DEPARTMENT OF THE ARMY

CORPS OF ENGINEERS

OMAHA DISTRICT

CONTRACT NO. DA-25-066-eng-3452

JOB 1113

OCTOBER 25, 1955

The Ralph M. Parsons Company
617 South Olive Street
Los Angeles, California

PCM-1606
RGM:jm

FOREWORD

During the summer of 1954, several farmers located near the northwest boundary of the Rocky Mountain Arsenal reported that serious injury was done to their crops when well water was used for irrigation. There was a strong feeling among these farmers and others who were concerned with the problem that the injury was caused by some toxic substance in the underground waters, and that this toxic substance came from the Arsenal. The United States Army Corps of Engineers negotiated a contract with The Ralph M. Parsons Company to determine the most economical measures that could be taken to eliminate or minimize the possibility of contamination of underground waters by the various industrial wastes from the chemical operations at the Arsenal. A secondary phase of the contract was to attempt to determine if there were a toxic component in the water that could cause crop damage and if possible, to recommend corrective measures to eliminate this toxicity.

The primary phase of the work performed under this contract, concerning methods for disposing of the chemical wastes from the plants in the Arsenal, was completed and submitted to the Corps of Engineers on September 29, 1955, in a report entitled "Final Report, Disposal of Chemical Wastes, Rocky Mountain Arsenal".

This report supplements the above mentioned final report and deals with the problem of identification and detoxification of the component or components in the underground waters which caused the crop injury reported by the farmers. Qualified consultants in the fields of agronomy, plant pathology and analytical chemistry were called in to assist in the study of this problem.

The purpose of this report is to present our findings and those of our consultants, to analyze these findings, and to present a recommended course of action to be followed to develop a final solution to this problem. The reports of our consultants have been reproduced and appended to this report.

PCM-1606
RGM: jm

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The Evidence Pointing to Methyl Phosphonic Acid	12
Possible Remedies	13
RECOMMENDATIONS	15
APPENDIXES	
The Groundwater Pollution Problem of the Rocky Mountain Arsenal by Jesse D. Skoss, Ph.D., Consulting Agronomist	
Report of a Trip of Inspection, July 16, 1955 by Jess L. Fults, Ph.D., Plant Pathologist, Colorado A & M College	
A Plan of Research, by Jess L. Fults, Ph.D., Plant Pathologist, Colorado A & M College	
A Preliminary Report on Toxic Properties of Well Water from the Powers and Munson Farms, by Jess L. Fults, Ph.D., Plant Pathologist, Colorado A & M College	
Letter Report on Tests of Methyl Phosphonic Acid on Growing Plants, by W. S. Ryder, Ph.D., Camp Detrick, Maryland	
Analytical Report, by E.W.D. Huffman, Ph.D., Huffman Microanalytical Laboratories	

PCM-1606
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Analytical Data Sheets, by John Hem,
Geological Survey, U. S. Department of Interior

Letter Report on Selenium Analysis by Dr. Boland,
University of Colorado Medical School

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SUMMARY

1. A number of experts in the fields of agronomy, plant pathology and analytical chemistry were consulted on the problem of identification of the constituent of certain well waters which caused crop damage in 1954 and of correction of this toxicity. A qualified expert in each of the above fields was asked to actively participate in the work on this problem. The individual reports from these selected experts are appended to this report.
2. The phytotoxic constituent of the well water cannot be positively identified from present data. The common salts present in the water, e.g., sodium and calcium sulfates and chlorides, did not cause the damage suffered by the local farmers in 1954 although these salts may be the cause of present low fertility of some portions of land. Circumstantial evidence strongly indicates that methyl phosphonic acid, a component of the Plant No. 1 effluent, is the sought-for compound. No evidence was found to prove or disprove the theory that the damaging constituent originated in Shell Chemical Company's chemical operations.
3. A botanical research program was developed by Dr. Fults, of Colorado A & M College, to positively identify the damaging agent. This program could be carried out by the Colorado A & M Research Foundation within three years at an estimated cost of 7,500 dollars for the first two years. Initiation of this program is recommended.
4. On the theory that methyl phosphonic acid is the phytotoxic agent and that a large reservoir of contaminated water exists under the ground, a chemical research program is recommended to determine if methyl phosphonic acid can be removed from a dilute water solution by a practical method. This program should be started by assigning two research chemists to the problem for two months. At the end of two months the program should be re-evaluated.
5. Due to the varying salinity and toxicity of Mr. Powers' well water, a field research program is recommended to attempt to correlate water toxicity with a simple quality measurement such as electrical conductivity. This program would require approximately 1,000 manhours during the course of one year. The use of a commercial research firm to carry out this project would cost approximately 9,000 dollars. If such a correlation is developed, the effected farmers could have limited use of their contaminated well water.

PCM-1606
RM: jm

CONSULTANTS

List of Consultants

In the course of our study of the problem of identification and detoxification of the well water component which caused the crop injury, the following persons were consulted and the opinions of these experts have been considered in preparing this report:

1. Dr. Arthur S. Newman
Chief, Chemical Branch
Crops Division
Headquarters, Camp Detrick
2. Pfc William Ryder, Ph. D.
Assistant Plant Physiologist
Crops Division
Headquarters, Camp Detrick
3. Mr. Samuel Sass
Chemical Division
Chemical Corps, Chemical and Radiological Laboratories
Army Chemical Center, Maryland
4. Mr. Robert J. Brown
Chief Chemist
Great Western Sugar Company
Denver, Colorado
5. Dr. Robert S. Whitney
Agronomist and Department Head
Department of Agronomy
Colorado A & M. College
Ft. Collins, Colorado
6. Dr. Jess L. Fults
Plant Pathologist and Department Head
Department of Botany and Plant Pathology
Colorado A & M. College
Ft. Collins, Colorado
7. Dr. E.W.D. Huffman
Huffman Microanalytical Laboratories
Wheatridge, Colorado

PCM-1606

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8. Dr. Thad McLaughlin, Geologist
Quality of Water Branch
Geological Survey
U. S. Department of Interior
Denver Federal Center
Denver, Colorado
9. Mr. John D. Hem, Chemist
Quality of Water Branch
Geological Survey
U. S. Department of Interior
Denver Federal Center
Denver, Colorado
10. Dr. Jesse D. Skoss
Consulting Agronomist
310 S. Robertson Blvd
Los Angeles 48, California
11. Dr. L. E. Allison
U. S. Salinity Laboratory
U. S. Department of Agriculture
Riverside, California

FCM-1606

RCM: jm

DR. JESSE D. SKOSS

Agronomist

Education

College of Agriculture, University of California at Davis and Los Angeles
B.S., University of California, 1941
M.S. in agronomy, University of California, Davis, 1946
Ph.D. in botanical science, University of California, 1951

Professional Status and Membership

Alpha Zeta Agricultural Fraternity
Sigma Xi
American Society of Agronomists
American Society of Plant Physiologists

Experience

Los Angeles County Air Pollution District in charge of research on smog effect on agricultural products.

Consultant on turf grasses and ground covers, Disneyland Park Development, Anaheim, California.

Consultant to Chief Landscape Architect, University of California, Santa Barbara. Determination of grass and ground cover planting, soil preparation, drainage needs, irrigation distribution requirements of the new campus development.

Consultant to Caspar Burgi Company, Los Angeles, on soil contamination at Joseph Schlitz Brewing Company, Van Nuys, California. Remedied large landscaped area affected by chemical contamination.

Associate Editor of "Landscaping", trade journal for landscape architects and contractors, in fields of soils, irrigation, fertilization, weed control, turf grasses and ground covers.

Appointed Lecturer in Weed Control, Soils, Fertilization, and Irrigation - University of California Extension Division.

Active duty in U.S. Army - placed in charge of an Army farm of 122 acres on Oahu, Hawaii.

PCM-1606

RGM: jm

Wine chemist for Colonial Grape Products Corp., Elk Grove, California.

Farm Operations Division, College of Agriculture at Davis.

Performed chemical analysis on wines for the Viticulture Division,
College of Agriculture, Davis.

PCM-1606
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DR. E.W.D. HUFFMAN

HUFFMAN MICROANALYTICAL LABORATORIES

Analytical Chemist

Education

Ph.D. in chemistry, University of Colorado, 1940

Professional Status and Membership

American Association for the Advancement of Science
Sigma Xi

American Chemical Society

Chairman of Division of Analytical Chemistry

Chairman of Colorado Section

Council Member of National Society (6 years)

Committeeman on ACS Committees

Standardization of Apparatus

Balances and Weights

Program Planning

Council Committee on Publications

Experience

The business was established in 1936. From 1936-38 it was operated in Boulder, Colorado, from 1938-1952 in Denver, and 1952 to date in Wheatridge, Colorado.

The original services offered were limited to elementary organic quantitative microanalysis. This still is a basic and important part of the business. In the past few years we have expanded by accepting analytical investigations and chemical research where applied chemical analysis and physical measurements and the interpretation of these are a major part of the problem.

Our customers represent industries, schools, foundations and Government. A few examples of each - E. I. du Pont de Nemours & Co., Dow Chemical Co., General Tire & Rubber Co., Phillips Petroleum Co., Standard Oil (Ohio), Sharpe & Dohme, General Electric Co., etc.; Ohio State University, Purdue University, Princeton University, Yale University, University of Texas, University of Utah, University of Pennsylvania, etc.; Mellon Institute, Carbide & Carbon Co. (Oak Ridge); University of California (Los Alamos); Sandia Corporation. This is a representative list.

PCM-1606

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DR. JESS L. FULTS

Plant Pathologist

Education

B. Sc. Colorado A & M College, 1931

M. Sc. Iowa State College, 1932

Ph.D. in botany University of Nebraska, 1941

Experience

Head of Department, Department of Botany and Plant Pathology,
Colorado A & M College, Ft. Collins, Colorado.

Associate Agronomist, University of Texas, 1941-1945

Associate Agronomist, University of Colorado, 1939-1941

Associate Agronomist, University of Nebraska, 1935-1939

PCM-1606
RCM: jm

FINDINGS

Inspection of Damaged Lands

The farm land belonging to Mr. Jesse Powers were inspected during the summer of 1955 by Dr. Jess Fults, Head of the Department of Botany and Plant Pathology of Colorado A & M College and by Dr. Jesse Skoss, consulting agronomist, of Los Angeles. The portion of Mr. Powers' lands, where crops were damaged in 1954, still showed the presence of some phytotoxic constituent. The sparse growth of corn, oats and alfalfa in these affected areas and the type of weed which was growing could indicate, in the opinion of these experts, merely a high salt concentration in the soil. Chemical analyses of Mr. Powers' well water performed by Mr. Robert Brown, Chief Chemist for Great Western Sugar Company on June 3, 1954, showed an exceptionally high concentration of dissolved salts (3610 ppm). As this water was used to irrigate the sugar beets and the permanent pasture which were damaged, a large quantity of salt could still be in the soil.

A sample of the water from Mr. Powers' contaminated well was taken on July 15, 1955 and tested for toxicity by Dr. Fults at Colorado A & M. This water showed no toxicity in these tests. A full report of these tests was written by Dr. Fults and is appended to this report.

A second sample of this suspected well water was taken about August 15, 1955, and was analyzed by Dr. Huffman of Huffman Micro-analytical Laboratories for organic phosphorus and electrical conductivity. This analysis showed the water to be free of any type of phosphorus contamination. The specific conductivity of 2.42 (EC x 10³) of this sample is equivalent to a total dissolved solids content of under 2,000 parts per million. This water should be harmful only to the more sensitive crops and should have little effect on sugar beets.

Mr. Powers' description of the damage that occurred, and the reports of observations made by representatives of the Great Western Sugar Company in the summer of 1954, strongly indicated that the damage to the crops was not caused by the salts that were found in his well water. However, toxicity of the water coincided with high salinity. The damage to crops occurred in late spring when the total dissolved solids content of the water was about 3,600 ppm. The salt content of the water from this well dropped to 360 ppm in late September and this water was found to be non-toxic in tests conducted by Dr. Zimmerman of Boyce Thompson Institute, New Jersey.

PCM-1606

RGM:jm

None of the samples of water taken during 1954 was analyzed for methyl phosphonic acid because the analytical chemists were not aware of its possible presence nor of its possible phytotoxicity.

The individual reports of the investigation of this land by Dr. Skoss and by Dr. Fults are appended to this report.

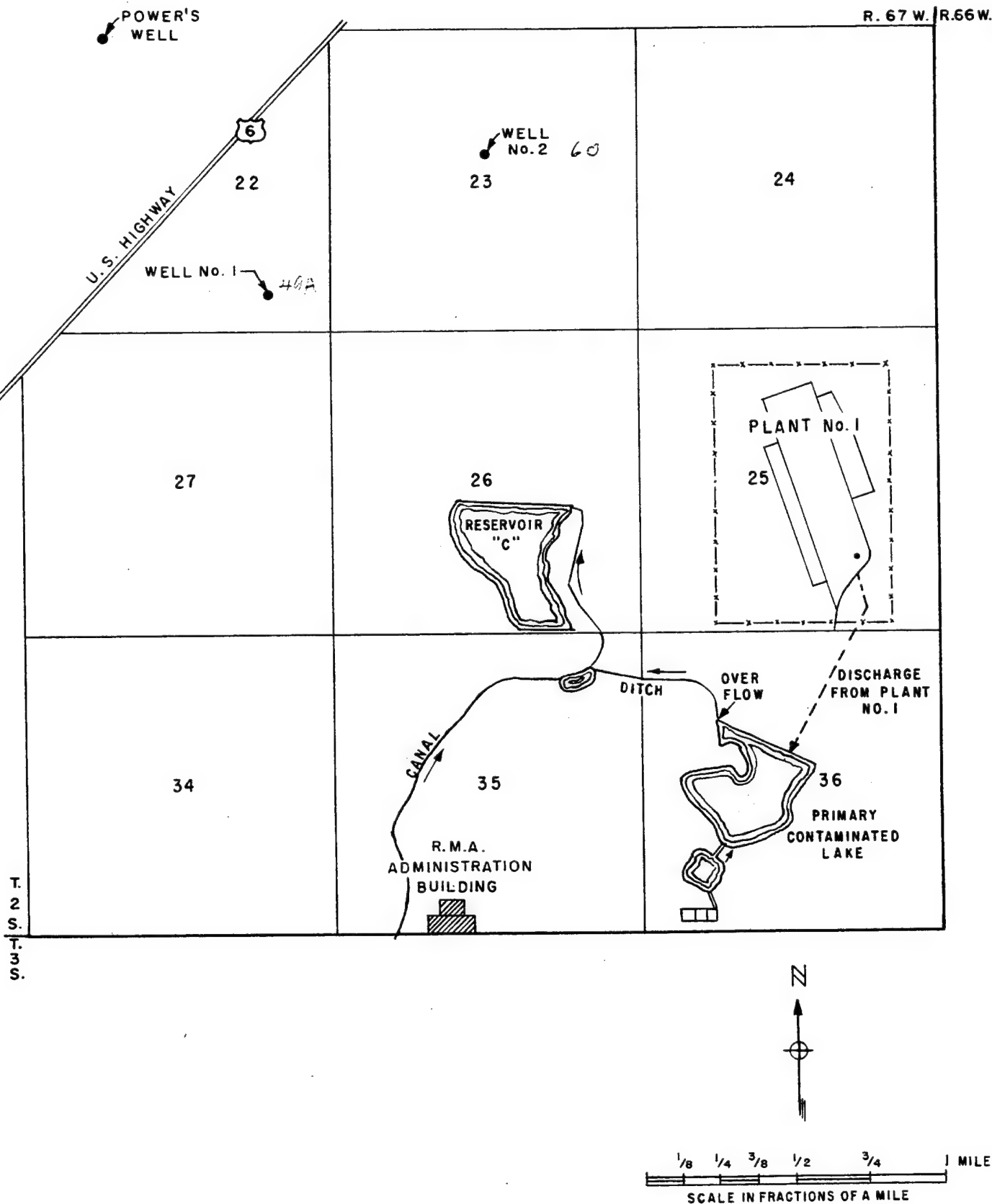
Inspection of Arsenal Lands

The land around the Arsenal's contaminated lakes shows the effect of the high salt and alkali content of the waters in the lake. Alkali-weed (*Kochia scoparia*) was growing close to and even partly submerged in the water. Perennial vegetation, particularly blue grama (*Bouteloua gracilis*), three-awn grass (*Aristida longiseta*) and buffalo grass (*Buchloe dactyoides*), grows in patches in the alkali soil around the lake. This vegetation is very salt tolerant and may even have developed a resistance to the other constituents of the lake waters.

Chemical Analyses of Arsenal Waters

Drs. Newman and Ryder of Camp Detrick, Maryland expressed a suspicion that the organic phosphorus compound present in the effluent from one of the chemical plants in the Arsenal could be toxic to vegetation. Mr. Samuel Sass of the Chemical and Radiological Laboratories at Army Chemical Center, as well as the chemists at Rocky Mountain Arsenal, thought that this organic phosphorous compound might be a salt of methyl phosphonic acid, $\text{CH}_3\text{PO}(\text{OH})_2$. A sample of this chemical was prepared in the Inspection Laboratory at the Arsenal and was submitted to Drs. Newman and Ryder at Camp Detrick for toxicity tests on growing plants. These tests showed that in doses over ten pounds per acre, methyl phosphonic acid can cause severe crop damage. The preliminary report of these tests is appended to this report.

Dr. Huffman developed an analytical scheme for detecting this chemical in dilute water samples. Water samples were taken from various places around the Arsenal (See Drawing No. 1113-AD3, page 10) and were analyzed for common salts by Mr. John Hem of the United States Geological Survey; for selenium by Dr. Bolton of the University of Colorado Medical School; and for phosphates, phosphites and organic phosphonates and for sulfides by Dr. Huffman. These analyses showed a very high salt content in the water at the following points: Plant No. 1 discharge, the contaminated lake, and wells No. 1 and 2. The selenium content of the waters was 0.015 ppm, which is normal for Denver area waters and is well below toxic limits. Phosphites were found in the Plant No. 1 effluent. ✓



THE RALPH M. PARSONS COMPANY LOS ANGELES	LAYOUT SKETCH OF ROCKY MOUNTAIN ARSENAL SHOWING LOCATION OF WATER SAMPLE POINTS	DRAWING NO. 1113-AD3	REV. <div></div>
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Methyl phosphonic acid was found in the Plant No. 1 discharge (960 ppm), the contaminated lake (640 ppm) and in surprisingly large amounts (180 ppm) in well No. 1. This well is located over a mile northwest of the secondary contaminated lake (Reservoir "C"). Well No. 2, located about a mile and a quarter north of Reservoir "C" was very salty but did not have any phosphorus compounds.

The detailed analyses of these samples and the analytical technique developed by Dr. Huffman for methyl phosphonic acid are given in the appended report from Huffman Microanalytical Laboratories and the data sheets from the Geological Survey.

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DISCUSSION

Several portions of Mr. Powers' land certainly show the presence of a material harmful to useful vegetation. If this land had been good fertile land prior to irrigation with well water in May 1954, as is stated by Mr. Powers, then the harmful material must have come from the well water. Mr. Powers' description of the damage to the crops and the observations of damage reported by Great Western Sugar Company probably cannot be blamed on the common salts reported in the analysis of this well water in 1954. It is, however, quite possible that the harmful material still present in his soil is not the original offending compound, but could be the common salts which could have accumulated from the past irrigations and which have not been leached out by rain or subsequent irrigation with good water.

It has been fairly well established that the salt content and the toxicity of Mr. Powers' well water varies widely with time. No confirmation has been found for the presence of a toxic material which disappears after short exposure to air, as was suggested by Great Western Sugar Company. It is our opinion that the toxic constituent is possibly quite stable. ✓

No evidence was found to indicate that the particularly damaging contaminant of the harmful waters originated in Shell Chemical Company's chemical operations at the Arsenal. One of their intermediate products, hexachlorocyclopentadiene, was found to be quite phytotoxic (Ryder's report from Camp Detrick), but analysis of the well waters for this compound was not attempted. Drs. Whitney and Skoss, agronomists, hold the opinion that there is little likelihood of this material moving more than a few feet underground, particularly in sufficient concentration to be toxic to plant life.

A definite answer as to what material or constituent of the well water did cause the crop damage could only be given after completion of a research program, such as is suggested in Dr. Fults' report in the appendix. This program could be undertaken by the Colorado A & M Research Foundation in Fort Collins, Colorado. Dr. Fults estimates this program would cost 7,500 dollars and would require a minimum of two years to complete.

The Evidence Pointing to Methyl Phosphonic Acid

Although the identity of the phytotoxic component of the damaging well water has not been definitely established, circumstantial evidence very strongly suggests that methyl phosphonic acid is this offending constituent.

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Methyl phosphonic acid and its sodium and calcium salts are very soluble in water. Salts of this acid are present in the Plant No. 1 effluent and in the contaminated lakes. The salts can move through the soil in relatively high concentrations without being immediately adsorbed by the soil, as evidenced by the analysis of the water from Well No. 1. Application of this compound to a wide variety of plant life in quantities of over 10 pounds per acre caused severe damage to the plants. The application to one acre of ground of one-half of an acre foot of water containing less than 8 parts per million of methyl phosphonic acid would contribute 10 pounds of the acid to the acre of ground. Mr. Powers did not recall precisely how much water was applied to his fields when his crop of sugar beets was damaged, however, several sprinklings could readily amount to over one-half an acre foot. If the water which Mr. Powers used on his crops in 1954 contained as much methyl phosphonic acid as did the water from the Arsenal's Well No. 1 in 1955, a dosage of over twenty times that found to be phytotoxic could have been applied.

If methyl phosphonic acid is found to be the crop damaging constituent, there is no way known at present to detoxify this compound or to remove it from the well water. Extremely severe chemical treatment is required to convert this material to harmless phosphates. Treatment with boiling, concentrated nitric and sulfuric acids or combustion with sodium peroxide at high temperatures are the techniques presently used in the laboratory for the conversion. These techniques could not be applied to well water.

The evidence suggests so strongly that methyl phosphonic acid causes the crop damage that it seems imperative that a chemical research program be started immediately to attempt to develop a practical scheme for removing this material from dilute water solutions. The ultimate cost of such a program is impossible to predict. The program could best be carried out by several research chemists. After a few months work, an answer could probably be developed or a prediction could be made of the additional costs and time required.

Possible Remedies

The Rocky Mountain Arsenal should take immediate steps to prevent the loss of additional waste waters containing methyl phosphonic acid to the underground water supply. This can be accomplished most practically and rapidly by installing asphalt membranes under new reservoirs, as was recommended in The Ralph M. Parsons Company "Final Report, Disposal of Chemical Wastes, Rocky Mountain Arsenal" dated September 29, 1955.

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Unfortunately, this procedure will still leave a great reservoir of contaminated water under the ground, which will possibly take years to dissipate.

The only remedy that appears practical at this time to eliminate the possible hazard of killing crops with the existing contaminated waters is suggested by the variation in salinity and toxicity of the water in Mr. Powers' well and the occasional availability of good water in the irrigation ditches.

When good ditch water is available to Mr. Powers or other farmers, it should be used to flood the affected portions of land to leach out accumulated water soluble salts. This technique would possibly restore fertility to this land. Mr. Powers' well water apparently is quite satisfactory at certain times and can be used for irrigation at these times. It would seem entirely possible to establish the safe periods for water use by a simple test of the water. As toxicity apparently varies directly with salinity, an electrical conductivity test would indicate quite simply and rapidly when the water is safe to use.

The value of such a program would, of course, require confirmation by field tests, but it seems to offer considerable promise as a course of action to be followed until the existing contaminated underground water is diluted to safe concentrations by natural dilution with rain water.

JENKINS
NBC

16 January 1956

"RECOMMENDATIONS OF THE H. PH. M. PARSONS COMPANY SUPPLEMENTARY REPORT"

1. Immediate measures should be taken by the Rocky Mountain Arsenal to prevent further contamination of underground waters with industrial waste, particularly those containing methyl phosphonic acid salts. The installation of asphalt membranes under reservoir areas as recommended in our final report on the disposal of chemical wastes from the Arsenal would accomplish this aim.

"2. A botanical research program should be initiated to identify the phytotoxic component of the crop damaging well water. The program outlined by Dr. Holt, in his report, would develop this information. This program could be carried out by the Colorado A&M Research Foundation within two or three years, at a cost for the first two years, estimated by Dr. Holt, at \$10,500.

"3. A chemical research program should be initiated to determine how methyl phosphonic acid can be detoxified or removed from a dilute water solution. It is recommended that two research chemists be assigned this problem for a period of two months. At the end of this period, additional time and cost required for this program could possibly be estimated. This program could probably best be carried out by the Chemical Corps Laboratory.

"4. A field research program should be initiated immediately to attempt to correlate simple measurement of water quality; such as, electrical conductivity with toxicity of the water from a well such as Mr. Powers. This program could be carried out by Arsenal personnel or a local university and would require routine sampling and testing on hot house plants. Such a program would require one man day, monthly or semi-monthly, plus daily watering and observation of the test plants for possibly a year. The cost of this program would be under \$9,000 based on estimates estimated at 1,000 hours time required during a year's program."

The Groundwater Pollution Problem
of the Rocky Mountain Arsenal by
Jesse D. Skoss, Ph.D., Consulting Agronomist

The Groundwater Pollution Problem
of the Rocky Mountain Arsenal, Denver, Colorado

Introduction - Water from a well on the farm of Jesse Powers, near Derby, Colorado, was used to sprinkle irrigate seedling sugar beets in the 1954 growing season. After several irrigations, covering a period of about one week, the beets were killed by some phytotoxic substance which was apparently a constituent of the irrigation water. ✓
Previous use of water from this well for irrigation purposes has produced normal, harvestable crops.

The proximity of the farm to the Rocky Mountain Arsenal cast suspicion on the arsenal as being the source of contamination. The arsenal was duly notified of this belief. Steps were then taken to determine the nature and cause of the damage to the Powers' farm crops. The aid of a number of public and private agencies were enlisted in the attempt of a solution to this problem. These agencies were:

A. Public

1. The Rocky Mountain Arsenal
2. The Corps of Army Engineers
3. Camp Detrick Biological Laboratories, Chemical Corps
4. The Geological Survey, U. S. D. I.
5. The Soil Conservation Service, U. S. D. A.
6. The Regional Salinity Laboratory, U. S. D. A.
7. The Agronomy and Plant Pathology Departments,
Colorado Agricultural and Mechanical College

B. Private

1. The Great Western Sugar Company, Colorado
2. Boyce Thompson Institute, Hoboken, N. J.
3. Huffman Microanalytical Laboratories, Wheatridge, Colo.
4. The Julius Hyman Division, Shell Chemical Company
5. The Ralph M. Parsons Company

These agencies have produced a mass of data which involved chemical analysis of numerous water samples from many sources in the affected area, as well as field and laboratory experiments and observations. A critical study of these findings leave much to be desired of them from a definitive point of view as regards the determination of the mechanism of damage. If this mechanism is known then its point of origin could be determined and corrected, with the Powers' farm thereby eventually returning to its original productive state.

The deficiencies in the collected data are due to the following:

1. Lack of factual, recorded information of the pattern of plant damage, with the factors which led to it. For example, the actual amount of water applied in the several irrigations and the number and periodicity of these water applications to the sugar beets is recollected from the farmer's untrained memory.

2. Time lag in which plant damage was initially reported and a proper study of the problem undertaken by scientific personnel.
3. The initial secrecy as to the nature of the possible contaminants of the groundwater with the result that these constituents were not analyzed for in the early water samplings.
4. The undirected method of approach to the problem by the numerous agencies which led to a partial obscuring of the agronomic aspects of the problem and improper sampling and/or analysis of samples taken.

The object of this report is to review the water analysis data and other laboratory findings; discuss observations made in an inspection trip; correlate the above in recommendations for corrective measures needed to restore the agricultural productivity of affected lands, or a testing program to determine these corrective measures.

Observations and discussion - The areas of the Powers farm which had grown the sugar beets which had been killed still evidenced the presence of some phytotoxic substance in the soil. The field had been plowed and planted to field corn for the 1955 season. The emergence was very poor with little survival. Scattered individual plants were severely stunted and scorched with the leaves inrolled as though suffering from lack of water and high salinity. Weed growth was generally sparse and halophytic in nature. Numerous bare areas or slick spots were present. An alfalfa field which had been partially flooded by water drained from the affected area had areas where the alfalfa had been killed out; the surviving plants appearing stunted in growth.

An analysis of the Powers well water had not been made at the time of injury to the sugar beets. The earliest analysis was reported by Robert J. Brown of the Great Western Sugar Company laboratory on June 3, 1954. The east well which was the one supplying the toxic irrigation water was very high in total solids, 3,610 ppm. Chloride content was 1,430 ppm, and sodium was 265 ppm. Calcium and magnesium as chlorides was 2,237 ppm. Phosphate was qualitatively reported present - after acid digestion. The specific conductivity of the water was not reported.

The next available analysis of waters taken from the Powers farm was reported by John D. Hem of the Geological Survey, U.S.D.I. on December 6 and 7, 1954. The well in question surged after five minutes of operation, analyzed 235 ppm of sodium, 1,010 ppm chloride and had a specific conductance of 3.88 ($EC \times 10^3 @ 25^\circ C.$). An adjacent stock well water analyzed 219 ppm sodium, 760 ppm chloride, with a specific conductance of 3.43. Water from this well was also reported to have "killed grass and flowers" and to have caused scouring in young calves. The scours was said to have cleared up when the calves were removed to another area of the farm and given water from a different source which was potable.

The Geological Survey also reported on analyses of water samples (Dec. 3, 1954) taken on R.M.A. property. These were of water from test holes and existing wells located in a more or less direct line between the Powers farm and the disposal ponds on arsenal property. Sodium, chloride and specific conductance varied somewhat but were, in all cases, extremely high. The range in magnitude of these two components were from 1,770 to 3,250 ppm for sodium, and 3,220 to 4,850 ppm for chloride. Specific conductance was from 10.5 to 15.1. Analysis for organic forms of phosphorus was not made.

It is clear that a pattern of increasing salinity and soluble salt content of the ground water exists from the Powers farm to the disposal ponds at the arsenal. These analyses show a more or less straight channel of movement of contaminated groundwater with these soluble ions, as evidenced by analysis of these numerous samplings. ✓

Recent analysis of waters from the arsenal are illuminating as to the sources of contamination. Selected components from the various sources are listed in Table I.

Table I
Selected chemical components and properties of analyzed water obtained from various sources on R. M. A. property

Source	Sodium ppm	Chloride ppm	pH	Specific conductance EC x 10 ³ @ 25° C.
Raw process water (dinner water)	128	160	8.0	1.44
Chemical plant discharge	3,340	3,230	11.4	16.50
Upper contaminated lake near overflow	3,480	3,530	9.8	14.20
Sample from well # 1	2,470	4,380	7.9	13.30
Sample from well # 2	1,790	4,570	8.0	14.30

(Analyzed by John D. Hem, Geological Survey, U.S.D.I., dated August 24, 1955)

The above data point to the extremely poor quality of the water from the chemical plant discharge on. This is beside the probable existence of constituents, namely methylphosphonic acid and its salts and certain chlorinated hydrocarbons (Pl62) in the water which were not analyzed for. The poor quality of the water is brought out when considered in the light of standards of quality for irrigation water, Table II. ✓

Table II
Standards for irrigation waters*

Water class	Conductance EC x 10 ³ @ 25° C.	Salt content	
		Total ppm	Per acre foot tons
Class 1 ¹	1 or below	700	1
Class 2 ²	1 - 3	700-2,000	1-3
Class 3 ³	3 or above	2,000	3 plus

*

Magistad, O.C. & Christiansen, J.E.: Saline soils, their nature and management, U.S.D.A Circ. 707, 1944.

- 1 Excellent to good, suitable for most plants under most conditions.
- 2 Good to injurious, probably harmful to the more sensitive crops.
- 3 Injurious to unsatisfactory, probably harmful to most crops and unsatisfactory for all but the most tolerant.

The wastes in aqueous solution discharged into the arsenal disposal ponds over a period of years amounted to thousands of tons. These disposals indicate the probable source of the groundwater contamination as originating at the disposal grounds of the arsenal. Table III lists the materials and approximate amounts of each (information source was Mr. R. G. McChrystal, of The Ralph M. Parsons Company of Los Angeles).

Table III
Materials discharged into the R.M.A. disposal ponds

Material	Amount
1. Lewisite (arsenic base)	Considerable
2. Arsenic trichloride	5-10 tank cars, 40-50 tons each
3. Mustard gas (thiodiglycol)	Many tons
4. White phosphorus	Less than ten tons
5. Phosphites and phosphates	Unknown amounts
6. Chlorides, caustic soda, lime	Thousands of tons
7. Sulfates and acetates	Several hundred tons
8. Organics from chlordane and dieldrin	One ton
9. Isopropyl alcohol	30-50 tons
10. Hydrofluoric acid or sodium fluoride	30-50 tons
11. Methylphosphonic acid and sodium and calcium salts	100-200 tons
12. Aluminum chloride	Several hundred tons

On August 19, 1955 the Huffman Microanalytical Laboratories of Wheatridge, Colorado, reported on an analysis of water samples for phosphates, phosphites, and organic phosphates (organic phosphonates) by difference). These samples were drawn from the plant intake, plant discharge, primary contaminated lake, wells number 1 and 2 on R.M.A. property, and an unspecified well on Powers' farm. The analyses reported as methylphosphonic acid are as follows: plant discharge water - 960 ppm; primary contaminated lake - 640 ppm; well number 1 - 180 ppm. All other samples were negative for this constituent. Well number 1 is approximately 2-1/2 miles from the primary contaminated lake; the Powers' well is 3-5/16 miles. The initial damage to the sugar beets occurred in 1954 and no analysis was made at that time for methylphosphonic acid in the Powers' well water. The specific conductivity of Powers' well water was 2.42 as determined at the time of the Huffman report. In view of the solubility of methylphosphonic acid and its calcium and sodium salts, and its recovery from the groundwater at well number 1, it is conceivable that it might have been present in the groundwater at Powers' farm at the time of initial crop damage in 1954.

Tests were conducted at Camp Detrick, Maryland in which the phytotoxicity of methylphosphonic acid and hexachlorocyclopentadiene (Pl62) to plants was explored. These two compounds were suspected as being possible constituents of the irrigation water which caused the sudden injury to the sugar beets. These tests were reported on by Mr. William S. Ryder, Jr., Plant Physiology Assistant at Camp Detrick, on August 16, 1955.

The tests were a standard foliar spray application at 0.1, 1.0, and 10.0 pounds per acre rate for each of the compounds. Test plants were black valentine bean, soybean, morning glory, radish, oat and rice.

At the 0.1 pound rate the methylphosphonic acid caused only a slight stunting of the oat. At the 1.0 pound rate the test plants exhibited slight formative effects, slight contact injury resulting in necrosis of small leaf areas, slight chlorosis, and to the oat, slight stunting. At the 10.0 pound rate the test plants exhibited very severe contact injury, moderate formative effects, severe stunting and death to some of the test plants. The herbicidal nature of this compound was as a contact herbicide rather than that of a growth regulating herbicide.

Phytotoxicity tests of compound P 162 at the 10.0 pound rate produced results very similar to those for methylphosphonic acid with the exception that there were no formative effects. The former compound was said to be somewhat more potent than the latter. This is not borne out by the data describing the plant injuries in the report, which is somewhat contradictory.

Well established sugar beets are among the most tolerant of agronomic crops to high salinity concentrations in the soil or irrigation waters. Seedling sugar beets are not tolerant to high salinity and can be readily injured. However the rapidity with which the sugar beets were killed cannot be attributed to the salinity of the soil or water. Damage by salts is generally gradual with burning appearing along the leaf margins which later becomes necrotic. Beets would be much more sensitive as seedling plants (such as the Powers' beets were said to be) to other phytotoxic agents than at later stages of development. ✓

Compound P 162 was not analyzed for in the numerous water analyses which were made. It is doubtful if it could be recovered in the groundwater. Methylphosphonic acid, on the other hand, does possess the property of mobility in the groundwater as evidenced by the Huffman report. ✓ The phytotoxicity tests conducted at Camp Detrick indicate that ten pounds per acre of methylphosphonic acid is phytotoxic to growing plants and can cause damage severe enough to result in their death.

It is not known what volume of water was applied to the beets. Several irrigation applications were reported to have been made by Mr. Powers. If one acre foot of water per acre had been applied to the beets then a content of 3.68 ppm of methylphosphonic acid in the water would be sufficient to furnish ten pounds of the acid to each acre. If the volume of irrigation water had been less than one acre foot per acre a proportionately greater concentration of the acid, of necessity, would be required. The rapidity with which the beets were wiped out and subsequent damage by waste waters to the adjoining alfalfa field would indicate that a relatively high concentration of phytotoxic agent had been applied.

Recommendations - A simple test could be set up to identify the agent causing the plant damage. Sugar beets could be grown in pots filled with soil from one of the uncontaminated fields of the subject farm (the soil being as similar to that of the affected field in texture and type), as well as soil from the contaminated field. After a period of growth corresponding to that of the original stand of beets compound P 162 and methylphosphonic acid and its salt derivatives could be applied in varying concentrations in water to replicates of beets grown in clean soil. Applications of chemicals should be applied foliarly as well as through the soil. Beets grown in the contaminated soil if showing injury similar to that of treated beets would indicate possible soil residuum effect of the causal agent. The contaminated soil could then be analyzed for the culprit. The solubility of methylphosphonic acid would probably preclude its remaining in the soil for any length of time. The treated soils could have serial experiments performed, i.e., growing beets in the soils and treating with varying amounts of water to determine the rate of removal of the offending compound.

Water from the offending well or wells should be analyzed for these constituents. If these compounds are found to be present the water should be used to irrigate newly established seedlings and observations made for phytotoxic effects.

The Robert J. Brown report indicated the rapid change in total salt content of the water of Powers' irrigation wells. A ten-fold decrease was noted in a relatively short period of time; from an injurious water of about 3,000 ppm of salt to one of about 300 ppm which is a good water. ✓ With fluctuations of this magnitude it may be possible to determine the quality of irrigation water by a simple periodic specific conductance test. The water should not be used when it reads above the average for uncontaminated well waters of the area.

The current poor growth of the corn and the presence of numerous bare or slick spots would indicate that the affected field has become salted by the use of highly saline irrigation well water. This can be determined readily by means of a specific conductance test on soil extracts of a number of field samples, keeping the samplings individualized as to horizons as well. The exchangeable bases, sodium, calcium and magnesium should be determined as well as anion content of chloride, carbonate, bicarbonate, sulfate, etc. If the soil is deflocculated due to high sodium content, and saline due high soluble salt then reclamation would be a relatively simple procedure.

Reclamation could be effected by the following procedure:

1. Deep chiseling so as to effect good sub-surface drainage.
2. Application of lime so as to furnish sufficient calcium to replace the sodium on the base exchange complex.
3. Possible addition of soil sulfur to acidify the soil and assist in the replacement of the sodium by the calcium.

4. Leaching out of the replaced sodium beyond the depth of normal rooting of crop plants using water of good quality. (It appears that the ditch water from the Platte river is of a quality that is desirable for this purpose).

If soil analysis determines that the affected field is saline only, with sufficient dibasic cations to counteract any sodium present, then reclamation could properly be effected by steps one and four above.

Respectfully submitted

Jesse D. Skoss

Jesse D. Skoss

October 17, 1955

PCM-1606
RGM: jm

Report of a Trip of Inspection, July 16, 1955
by Jess L. Fults, Ph.D., Plant Pathologist,
Colorado A & M College

Rocky Mountain Arsenal Water Contamination Problem - Report of a trip of
inspection July 16, 1955

Jess L. Fults
Botany and Plant Pathology Department
Colorado A & M College, Fort Collins,
Colorado. September 26, 1955

I. Inspection of Rocky Mountain Arsenal

The morning was spent at the office of Mr. R. G. McChrystal, representative of the Ralph M. Parsons Company, Los Angeles, California and in the office of Mr. G. F. Donnelly, Chief Engineer (Phone Atlas 80711, extension 6240), U. S. Army Engineering Corps. At this time opportunity was afforded to inspect maps of the Arsenal showing centers of operation, lakes where waste chemicals have been dumped for the past several years and the canals which supply incoming water and drainage. During this period an opportunity was given to inspect the complete files in Mr. Donnelly's office on the water contamination problem located to the northwest of the Arsenal.

At about 11:30 A. M. an inspection was made of the area where chemical effluents from the Shell Oil Company operations and the Biological Warfare unit are currently being placed. The following, which may have significance, was observed:

- (1) Alkali-weed (Kochia scoparia) was found growing all around the contaminated lake area - in fact, it grew right up to the water level line of the lake. Around the lake shore which obviously varied in extent from time to time, much of the perennial native vegetation was dead - particularly blue grama (Bouteloua gracilis), three-awn grass (Aristida longiseta) and scattered patches of buffalo grass (Buchloe dactyoides). This decline of the native vegetation around the shore of an intermittant lake is not unusual and would be expected to occur whether chemical effluents from a chemical manufacturing plant were being dumped or not. The Panhandle area of Texas, from Lubbock north, is dotted with thousands of such intermittant lakes where the native vegetation along the shore-lines shows variation from year to year depending on the level of the water in the lakes (locally called "playas").
- (2) In the vicinity of the effluent from the Shell Oil Company area, the air was foul with a sharp pungent odor. It did not seem to be particularly irritating to the eyes even though the odor was very strong. Whether or not the air contained contaminants which might be toxic to crop plants needs to be determined.
- (3) The area to the northwest of the main contaminated lake, known as "the straw-bottomed lake" at times has received overflow from the main contaminated lake. The lake might be the key to the entrance of toxic materials into the underground waters of the area. The fact that it is called "the straw-bottomed lake" is suggestive that waters entering

quickly disappear into the subsoil. If there is a peculiar formation under the "straw-bottomed lake" which would allow free flowing water to percolate through to the impervious layer which apparently occurs at a depth of about 40 feet and which slopes to the northwest of the arsenal(?) this could account for an intermittent appearance of toxic materials in the well waters northwest of the Arsenal. It might be profitable to correlate the times of overflow from the main contaminated lake into the "straw-bottomed lake" with the time of appearance of toxic materials particularly in the well at the Powers' farm. This would presume that records have been kept of the times of overflows from the contaminated lake and the time of appearance of toxic water in the Powers' well or other wells. As a precautionary measure it is suggested that the "straw-bottomed lake" be puddled or otherwise be made impervious, if occasional overflow from the main contaminated lake is necessary.

(4) There would seem to be little or no chance for toxic materials to move through the soil to a depth of 40 feet (about the average depth of the irrigation wells to the northwest of the contaminated lake) and laterally, a distance of some two miles because of the adsorptive and absorptive power of the soil. Providing that it can be shown that the actual effluent from both the Shell Oil Company and from the Biological Warfare operations is toxic to crop plants - and there is no conclusive data on this which I have seen - then soil filtration tests should be made to determine the maximum depth of soil column through which plant toxicants can pass. From our experience with various kinds of chemical soil sterilants used as herbicides and fungicides, it should not be more than a few feet at the most.

2. Inspection of farm lands in the area northwest of the Rocky Mountain Arsenal

The afternoon was spent inspecting the irrigation water damage at the Powers' farm and on the adjacent Munson farm to the north of the Powers' farm. Some of our observations were as follows:

- (1) We observed positive evidence of damage to an oat crop immediately north of the bad well near the Powers' residence. Treatment consisted of late well irrigation of approximately 1 acre of beets in the fall of 1954 (according to Mr. Powers) followed by a crop of oats in the spring and summer of 1955. The oats on the area watered with well water in the late fall averaged 6 inches tall. On the area watered with ditch water (origin outside the Powers' farm), the oats averaged 16 inches tall. On both the damaged area and the undamaged area plants produced fully filled out seed. Whether the viability of the seed was affected is not known.
- (2) It was observed that the farm immediately south of the Powers' farm was using well water on a crop of corn (?) without evidence of injury.

- (3) The farm immediately north of the Powers' farm was inspected for evidence of injury from irrigation well water. The evidence was not conclusive. Crops being irrigated were carrots, onions, and alfalfa. A rather large carrot field on the east side of the farm appeared suspect. This field had been row-irrigated with well water in alternate rows. In parts of the field there was a big difference in the height of the carrots in alternate rows but whether the effect was due source of water or not was problematical and inconclusive.

PCM-1606
RCM: jm

A Plan of Research, by Jess L. Fults, Ph.D.,
Plant Pathologist, Colorado A & M College

A plan of research to obtain an answer to the problem "What is the evidence that operations at the Rocky Mountain Arsenal are or have been responsible for the contamination of irrigation wells located in the general area two to five miles north-west of the Rocky Mountain Arsenal"

Jess L. Fults
Department of Botany and Plant Pathology
Colorado A & M College, Fort Collins,
Colorado. September 30, 1955

Introduction

A review of the correspondence, information, and data on file in the office of Mr. G. F. Donnelly, Chief Engineer, U. S. Army Corps of Engineers, Rocky Mountain Arsenal has been made.

As of July 16, 1955, there appears to be no conclusive data which would fully support either positively or negatively the idea that the cause of irrigation wells going bad to the northwest of the Rocky Mountain Arsenal is due operations on the grounds of the Arsenal.

A primary premise of previous explorations has been that the irrigation wells in question have gone bad because of increased salinity or increased total salt content (see files in Mr. Donnelly's office). The validity of this primary assumption is in doubt for the following reasons:

- (1) Dr. Russell Nelson, Great Western Sugar Company Research Experiment Station at Longmont, Colorado, in the summer of 1954 made up a water solution of equal salinity to that of the highest analysis for the Powers' well. This experimental solution was used to grow sugar beets. No phytotoxic or abnormal growth of the beets occurred.
- (2) During the period January 1, 1954 to September 1, 1954, the total salt content of the Powers' well showed a steady decline from about 3000 ppm to about 300 ppm but in October 1954, when this water was used to irrigate late sugar beets, plants turned yellow (Powers' observation), and the following summer (1955) there was serious injury to a crop of oats almost to the line where the previous crop of sugar beets had been late-watered once.
- (3) For many years it has been known that 2 percent salt (NaCl) plant sprays can be used as a selective chemical weed control in sugar beets without damage to the crop. In other words, sugar beets are highly resistant to both the Na^+ and Cl^- ions and are generally recognized as tolerant of alkaline soil conditions. This does not tally with the fact that sugar beets on the Powers' farm have been injured with well irrigation water applied late in the growing season if the important factor causing injury was high salinity.

Because of these reasons, it is suggested that the problem be attacked from a different approach.

I. Statement of the problem

1. Does the effluent from the Shell Oil Company operations at the Rocky Mountain Arsenal contain substances which are toxic to sugar beets, oats, alfalfa and corn?

In order to answer this question, several sub-questions must be answered.

- (a) Assuming that this effluent does contain substances toxic to crop plants, what is the threshold value (dilution ratio in distilled water) for the several plants?
 - (b) Are there seasonal variations in the threshold values for the above crop plants?
 - (c) Do these threshold values change after various periods of time?
2. Does the effluent from the Biological Warfare operations contain substances which are toxic to sugar beets, oats, alfalfa and corn?
 - (a))
 - (b)) Same as for 1 above.
 - (c))
3. Does the "average" water in the contaminated lake contain substances which are toxic to sugar beets, oats, alfalfa and corn?
 - (a))
 - (b)) Same as for 1 above.
 - (c))
4. Does the water from the "bad" well at the Powers' farm contain substances which are toxic to sugar beets, oats, alfalfa and corn?
 - (a))
 - (b)) Same as above 1
 - (c))
 - (d) What are the volume-time relationships of the water from this well?

Preliminary evidence has shown quite clearly that one application of this water sampled July 16, 1955, has no damaging effect on either sugar beets or tomatoes. See attached report of tests.
 - (e) Does this water cause injury when sprayed repeatedly on the tops of crop plants?
 - (f) Does this water cause injury when exclusively applied to the roots of crop plants? What volume is necessary?
 - (g) Are there soil-water interactions which can account for the toxicity of this water to plants?
5. Assuming that the effluents from the Shell Oil Company operations and the Biological Warfare operations contain substances toxic to crop plants?
 - (a) Are these toxicants removed by percolation through soil columns?
 - (b) What is the maximum soil column depth through which these toxic substances will pass?
 - (c) What are the toxic substances being dumped into the "contaminated lake"? What are the threshold values for these substances against crop plants already mentioned?

6. Assuming that answers to the sub-problem in 5 above can be found then:

- (a) Do these specific toxic substances occur in the water of the bad well on the Powers' farm? Other wells in the vicinity?
- (b) If specific toxic substances are found, do they occur at any time during the growing season at concentrations sufficient to cause the damage already observed from previous experience on the Powers' farm?

III. Procedure

The details of procedure can be worked out later if it is agreed that the line of reasoning and research is sound and acceptable. The general plan of procedure would be to take periodic samples of 1) effluents, 2) contaminated lake water and, 3) water from "bad" wells; transport to our laboratories at Colorado A & M College; set up adequate replicated tests in our greenhouses under controlled conditions; follow up with tests on our college farm here at Fort Collins and with tests on the land near the Rocky Mountain Arsenal (Powers' farm?) where damage from well water is evident. At the conclusion of tests a complete report will be written and submitted to interested parties.

IV. Anticipated time for completion

A minimum of two (2) years with contractor's option to renew for a third year.

V. Estimated Annual Budget

	<u>Tentative Assignment</u>	<u>Salary</u>	<u>Project Share</u>
Colo. A & M Research Foundation			
Professional salaries			
Fulfs, Jess L. Plant Physiologist; Project Leader	(1/12 time)	\$7400.00	\$616.67
Payne, Merle G. Biochemist	(1/12 time)	4600.00	383.33
Technical salaries			
One fulltime Research Assistant - Plant Physiologist with minor interest in soils and biochemistry			5000.00
Other research labor - part time as needed			500.00
Supplies and expendable materials			500.00
Miscellaneous services (Colo. Agr. Research Found. 5% institutional overhead charge, stenographic, accounting, transportation and communications cost			500.00
TOTAL ANNUAL CAMRF BUDGET			<u>\$7500.00</u>

VI. Consultant Services

No fee would be expected for time spent on this project during regular College working hours during the period of a CAMRF contract. For any time spent outside regular duty hours I would expect to be paid \$100.00 a day and expenses. Presenting evidence in a court of law, extended travel, or actual time over and above 26 working days a year would be on a consulting basis with a corresponding salary adjustment from the College.

A Preliminary Report on Toxic Properties
of Well Water from the Powers and Munson Farms,
by Jess L. Fults, Ph.D., Plant Pathologist,
Colorado A & M College

A preliminary report on the toxic properties of well water from the Powers and Munson farms located 2 miles northwest of the Rocky Mountain Arsenal, Denver, Colorado.

Jess L. Fults, Plant Physiologist
Colorado A & M College, Department
of Botany and Plant Pathology,
Fort Collins, Colorado

Date and method of water collection

Collected from the Powers' "bad" well, 100 yards west of the Powers' farmhouse, 4 P. M. July 16, 1955. Mr. Powers started pump and water ran for 10 minutes after which two 1-liter samples were collected in new, unused plastic bottles. Samples were taken to Fort Collins and there used in two series of tests:

- Series I. Water used to moisten seedling sugar beets and tomatoes.
Series II. Water used in a small field test as a plant spray on two different sizes of sugar beets.

Results:

Series Ia. Sugar beets. Greenhouse test.

Sugar beet seed was sown in rows in a greenhouse wooden flat in a Pasteurized greenhouse soil mixture on July 19th; when seedlings were 8 days old, the flats were allowed to become quite dry for 2 days; on the 10th day, July 29th, they were watered once with Powers' well water and thereafter as needed with Fort Collins tapwater. The plants were watched closely after treatment up until August 19. At no time were any pronounced toxic reactions observed. In fact, in this limited test there was less damping-off (fungus attack) of seedlings and slightly better growth in the flat receiving the Powers' well water than in the controls. Photographs of the condition of the plants on August 9th are attached

Series Ib. Tomatoes. Greenhouse test.

The experiment on tomatoes was handled in the same manner as the sugar beets with the same results. See photographs attached.

Series II. Sugar beets. Field Test.

Tests were made at the College Bay farm, located 3 blocks west and 1/4 mile south of the intersection of College Avenue and Prospect Street, Fort Collins, Colorado. Tests were located in the southwest 1/4 of the 5-acre test block assigned to the Botany and Plant Pathology Department.

Test Block A. Sugar beets were 10 inches tall at time of treatment. Twenty feet of row was sprayed for each treatment as follows: Sprayed July 19, 1955.

- Row 1. Leaves sprayed with distilled water.
2. Leaves sprayed to runoff with Powers' well water.
3. Leaves sprayed with distilled water.
4. Leaves sprayed to runoff with Munson's well water. (From well 1/2 mile north of Powers' farm.)
5. Control - no spraying.

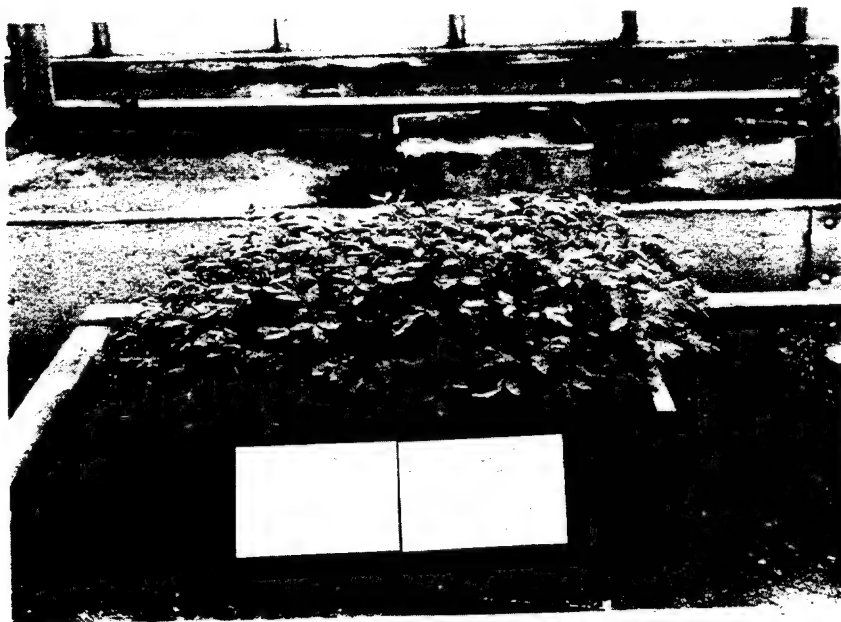
Test Block B. Sugar beets were 6 inches tall at time of treatment. Twenty feet of row was sprayed July 19, 1955 for each treatment as follows:

- Row 1. Control - no spraying.
- 2. Leaves sprayed with distilled water.
- 3. Leaves sprayed to runoff with Powers' well water.
- 4. Leaves sprayed to runoff with distilled water.
- 5. Leaves sprayed to runoff with Munson's well water.

Observations were made twice a week until September 15th. In no case was there any toxic response under the conditions of these tests.



FULTS POINT PLANT PATH COLO ARIZ FT COLLINS, COLO.





Letter Report on Tests of ^{sodium} Methyl Phosphonate^{ate}
Acid on Growing Plants, by W. S. Ryder, Ph.D.,
Camp Detrick, Maryland

HEADQUARTERS CAMP DETRICK
FREDERICK, MARYLAND

CMLCD-10-C

16 August 1955

Mr. R. G. McChrystal
Project Engineer
The Ralph M. Parsons Co.
617 South Olive Street
Los Angeles 14,
California

Dear Mr. McChrystal:

Since last we corresponded, a few test results have been evaluated and are enclosed herewith. We have been unable to do anything with regard to inorganic phosphites in as much as such compounds are not available here. I have ordered a sample of phosphorous acid with the idea of making some inorganic salts for testing. The material should arrive any day now so that work can begin in the very near future. As soon as we have any information you will be brought up to date immediately.

Your sample of methanephosphonic acid was tested in our regular screening program. As I indicated to you on your visit to Detrick, we test all compounds by means of a foliar spray application at rates of 0.1 and 1.0 pound per acre on six different crop species: Black Valentine bean, soybean, morning glory, radish, oat and rice. At 0.1 pound per acre methanephosphonic acid produced no evidence of herbicidal activity except a very slight stunting on oat. At 1.0 pound per acre, the following results were observed:

- BV bean - slight formative effect
- Soybean - slight contact injury and formative effect
- Morning glory - slight chlorosis and necrosis
- Oat - slight stunting

This compound was also tested at the rate of 10.0 pounds per acre with the following results:

- BV bean - severe contact injury, moderate formative effect, moderate stunting, two of the four plants died.
- Soybean - very severe contact injury and severe stunting
- Morning glory - same as soybean
- Radish - severe contact injury
- Oat - severe contact injury
- Rice - severe contact injury and stunting

These results while only preliminary indicate that at a rate of 10.0 pounds per acre this compound possesses a fairly high degree of phytotoxicity. Its action is like a contact herbicide rather than a growth

PCM-1606
RGM: jm

Analytical Data Sheets, by John Hem,
Geological Survey, U. S. Department of Interior

16 August 1955

regulating compound. The fact that some formative effects were noted on the bean species indicates some slight growth regulating activity which needs further clarification. In order to test the effectiveness of this compound as a soil contaminant, applications were made to BV beans and radishes at rates of 1.0, 5.0, 10.0 and 100.0 pounds per acre. At the highest rate the beans showed slight chlorosis and stunting, and the radishes showed a slight malformation of the bulbous root. It is not unusual that considerably higher rates are needed for activity when using soil applications. Further testing with both spray and soil applications are needed before final conclusions can be drawn.

Fairly recently we obtained a sample of hexachlorocyclopentadiene from Dr. E. S. Feichtmeir of Shell Development at RMA. He has supplied us with some of the data on mammalian toxicity which you undoubtedly already have obtained. This compound (Pl62) was tested in our regular screening program and showed no herbicidal activity at rates of 0.1 and 1.0 pound per acre. At the rate of 10.0 pounds per acre the following results were obtained:

- BV bean - very severe contact injury
- Soybean - same as above
- Morning glory - severe contact and slight stunting
- Radish - very severe contact injury and moderate stunting
- Oat - severe contact injury
- Rice - slight injury

These results are very similar to those for methanephosphonic acid except that Pl62 gives no evidence of a hormone or growth regulating type activity. Pl62 appears to be a rather potent contact type herbicide. This material has been used successfully for some time by the Oregon Agricultural Experiment Station as a soil sterilant and aquatic herbicide. Pl62 has been used here in 1, 5, and 15% solutions of emulsifiable concentrate in Diesel oil as a defoliant for woody species. At rates of 18.3 gallons per acre applied on several species of woody plants, contact injury has ranged from slight to very severe and defoliation has been noted from 25% to 100%.

When applied to the soil at rates of 10.0 and 100.0 pounds per acre, Pl62 caused moderate to severe stunting of BV beans. At the higher rate, the beans showed a moderate formative response; while the radishes exhibited very severe stunting and severe necrosis.

Again these results are only preliminary. It would appear that Pl62 is somewhat more phytotoxic as a foliar spray compared to methanephosphonic acid. Pl62 is considerably more effective as a soil contaminant compared to methanephosphonic acid.

Very truly yours,

William S. Ryder, Jr.

William S. Ryder, Jr.
Plant Physiology Assistant

cc to Mr. G. F. Donnelly
WSR:cd

PCM-1606
RGM: jm

Analytical Report, by E. W. D. Huffman, Ph.D.,

Huffman Microanalytical Laboratories

HUFFMAN MICROANALYTICAL LABORATORIES

3830 HIGH COURT, P.O. Box 125

WHEATRIDGE, COLORADO

August 19, 1955

MICROCHEMICAL ANALYSES
SPECIAL PROBLEMS

E. W. D. HUFFMAN, Ph. D.

Analytical Report

(To the Ralph M. Parsons Co. as per P.O. #S-1329; req. #R.G. McC.)

The determination of orthophosphates, phosphites or hypophosphites, organic phosphonates and sulfide sulfur in six water samples taken from the Arsenal (Denver) and wells in the area. The specific conductivity of the water from the Jess C. Powers well.

Table I

sample description	orthophosphates mg P/ml method 1	phosphites hypophosphites mg P/ml method 2	total phosphorus mg P/ml method 3	organic phosphonates mg P/ml calculated	sulfide sulfur mg S/ml
plant intake	0.00	0.00	0.00	0.00	less than 0.0003
plant discharge	0.00	0.01	0.33	0.32	" " "
lake 1 discharge	0.00	0.00	0.18	0.18	" " "
well 1	0.00	0.00	0.06	0.06	" " "
well 2	0.00	0.00	0.00	0.00	" " "
well, Powersfront	0.00	0.00	0.00	0.00	not determined

Specific conductivity of water from Powers well: $242 \text{ mho} \times 10^{-5}$ at 25°C .

A. Phosphorus determinations:

Test values have been rounded to the nearest 0.01 mg. of phosphorus per milliliter - about one part in 100,000. Without further study, and appropriate masking or separations, values to 0.001 mg/ml are in question because of interferences such as the presence of silica, iron, etc.

At the 0.01 mg P/ml level: (1) There are no orthophosphates present in any of the waters tested (method 1); (2) only in the plant discharge was phosphorus found which could have been present as phosphite, hypophosphite or an organic phosphorus combination which could have been oxidized or hydrolyzed (orthophosphoric ester) to orthophosphate by ammonium persulfate (method 2); (3) In the plant discharge, lake 1 discharge, and well 1 significant amounts of phosphorus were found after the samples were subject to the strong oxidizing action of hot nitric and sulfuric acids (method 3).

The applicability of the methods is tabulated in table II. Known solutions of potassium dihydrogen phosphate, hypophosphorus acid and methyl phosphonic acid were used as test standards.

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MICROCHEMICAL ANALYSES
SPECIAL PROBLEMS

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August 19, 1955

E. W. D. HUFFMAN, PH. D.

Table II

	<u>method 1</u>	<u>method 2</u>	<u>method 3</u>
potassium dihydrogen phosphate	quantitative	quantitative	quantitative
hypophosphorous acid	negative	quantitative	quantitative
methyl phosphonic acid	negative	negative	quantitative

Orthophosphate is measured by all three methods; phosphites and hypophosphites by methods two and three, but not by method one; organic phosphonates by method three but not by methods one and two.

Column 4, table I, gives the difference between total phosphorus (column 3) and phosphorus plus phosphoric phosphorus (column 2). It is headed "organic phosphonates". However, to date no effort has been made to find positive proof of the existence of organic phosphonates in the water samples. Considering the sources of the water samples the presence of such compounds is entirely possible (also see table II). Positive proof could be given only by the separation and identification of equivalent amounts of such compounds. Further indirect evidence could be obtained by determining the magnitude of the organic carbon present (total carbon less carbonate carbon).

Possibly the most significant value reported is the "organic phosphonate" content of well 1 (0.06 mg/ml). This value has been checked thoroughly. Well contamination by commercial phosphate fertilizers cannot be overlooked. However, such materials should show positive tests for phosphorus by all three methods used, not just by method 3.

B. Sulfide sulfur:

No positive test for sulfide sulfur was obtained in any of the water samples examined (Table I). In order to set a limit the sensitivity of the test employed was determined. The test gave clearly positive results for sulfide sulfur in a concentration of 0.0003 mg/ml. (Organic sulfides, or disulfides were not measured.)

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MICROCHEMICAL ANALYSES
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E. W. D. HUFFMAN, PH. D.

Methods

A. Phosphorus:

Method 1. Three ml of water was pipetted into a 100 ml volumetric flask. To this was added 1.5 ml of concentrated sulfuric acid and the solution was diluted to about 65 ml.
Color development - see below.

Method 2. Three ml of water was pipetted into a 100 ml volumetric flask. To this was added one ml of 10% aqueous ammonium persulfate solution. The solution was heated on the boiling water bath for 30 minutes. It was then cooled and diluted to about 65 ml.
Color development - see below. *1.5 ml. of conc. H₂SO₄ added*

Method 3. Three ml of water was pipetted into a 30 ml Kjeldahl flask. To this was added 1.5 ml of concentrated sulfuric acid and 3-4 drops of concentrated nitric acid. The solution was boiled gently until the water had evaporated and then more strongly until the nitric acid had been expelled and fumes of sulfuric acid were visible. The solution was cooled, 3-4 drops of concentrated nitric acid added and heated again until fumes of sulfuric acid were visible. After cooling the solution was diluted and transferred to a 100 ml volumetric flask making the final volume about 65 ml.
Color development - see below.

Color Development for Methods 1, 2 and 3:

Reagents:

1.) Ammonium vanadate solution containing 0.20% vanadate. Cautiously add to 500 ml of boiling distilled water 2.35 g of ammonium meta vanadate and then 100 ml of dilute sulfuric acid (1:12). After cooling make the solution up to one liter.

2.) Ammonium molybdate solution containing 10% MoO₃. Dissolve 122 g of ammonium molybdate in 880 ml. of distilled water.

Procedure. To the solutions (about 65 ml) in the 100 ml volumetric flasks add: (1) 10 ml of the vanadate solution slowly with swirling followed by (2) 10 ml of the molybdate solution. Make the solutions up to the mark with distilled water, mix, and let stand 30 minutes. Read optical densities (compared to a blank) at 410 mμ. Determine quantities from a calibration curve.

B. Sulfide sulfur:

Test papers were moistened with a solution of sodium plumbate prepared by adding sufficient sodium hydroxide to a solution of lead acetate to dissolve the precipitate first formed.

The sensitivity of the test papers was determined by holding them over a boiling

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E. W. D. HUFFMAN, PH. D.

solution of acidified sulfide solution of known concentration. A concentration of 0.0003 mg S/ml was sufficient to give a good test (black coloration due to lead sulfide formation).

Water samples were acidified and tested in the same manner as the standard. No black coloration was observed.

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MICROCHEMICAL ANALYSES
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Miscellaneous Notes

1.) The samples from the plant discharge and from the lake 1 discharge contained insoluble material. This material was allowed to settle before samples were withdrawn.

2.) In the early stages of testing for phosphorus the method used in the Analytical Branch, Chemical Div., C. & R.L. for the determination of organic phosphorus and inorganic phosphorus was used. This method was discarded because of interferences from silica, iron, etc.

U. S. DEPT. OF THE INTERIOR -- GEOLOGICAL SURVEY

Statement of Water Analysis

Source _____ Chemical plant discharge sample
Location _____ Rocky Mountain Arsenal, Adams County, Colorado
_____ 1/4 _____ 1/4 _____ Sec _____ T _____ R _____ Field No. _____ Office No. _____

Date collected July 1955
Discharge _____
Temp. (°F) _____ Time A. M.
Collected by R. G. McChrystal

Type of well _____
 Depth (ft.) _____ Cased to _____
 Diameter (in.) _____
 Date drilled _____ Use _____
 W. B. F. _____
 Depth to water (ft.) _____
 Owner _____

Chemical components	ppm	epm
---------------------	-----	-----

Silica (SiO ₂)	7.4	
Aluminum (Al)	.1	
Iron (Fe) 1/ Sp. g.	1.005	
Manganese (Mn) 1/	0.00	
Calcium (Ca)	.8	0.04
Magnesium (Mg)	1.0	0.08
Sodium (Na)	3.340	145.24
Potassium (K)	9.0	0.23

Cations (open) 145.59

Bicarbonate (HCO_3)	170	15.66
Carbonate (CO_3)	349	20.52
CH		
Sulfate (SO_4)	336	7.00
Chloride (Cl)	3,230	91.10
Fluoride (F)	119	6.26
Nitrate (NO_3)	5.0	0.08
Phosphate (PO_4)	.4	

Anions (ppm) 140.62

Diff: Cations - anions, eqm 4.97

1' In solution at time of analysis

Physical characteristics and computed values

Dissolved solids (ppm)	9,180
Res. on evap. at 180°C	7,870
Sum	
Suspended solids (ppm)	
Hardness as CaCO ₃ (ppm)	
Calcium, magnesium	6
Total	6
Non-carbonate	
Specific conductance	16,500
(micromhos at 25°C)	11.4
pH	0
Color	100
Percent Na	

Oxidation potential
~~pH 5.000~~
~~4.971/5.000~~ = -6.0 mv

Radiochemical data

Beta-gamma activity (micro-	
microcuries per liter)	
Radium (Ra) (micro-	
microcuries per liter)	
Uranium (U)	
(micrograms per liter)	

Lab. No. 706 Approved by R. A. Wilson Date August 21, 1925

John W. Kern

Letter Report on Selenium Analysis by Dr. Boland,
University of Colorado Medical School

UNIVERSITY OF COLORADO
MEDICAL CENTER
4200 EAST NINTH AVENUE
DENVER 20, COLORADO

July 28, 1955

COLORADO GENERAL HOSPITAL
COLORADO PSYCHOPATHIC HOSPITAL
SCHOOL OF MEDICINE

Mr. R.G. McChrystal
c/o Ralph M. Parsons Company
617 South Olive
Los Angeles 14, California

Dear Mr. McChrystal:

The Public Health Bulletin publication in 1946 states the maximum permissible concentration of selenium in domestic water to be .05 ppm. Colorado General Hospital tap water has been found to contain between .01 and .02 ppm. The samples which you submitted were found to be as follows:

Sample No. 1 --- .010 to .015 ppm selenium
Sample No. 2 --- Less than .01 ppm selenium

We observed on analyses that Sample No. 2 contained comparatively high concentrations of other salts which we did not identify. These may be the cause of your difficulty.

If we can be of any further assistance to you in the determination of toxic materials in these waters or others, please let us know.

Yours very truly,

ROBERT F. BELL, M.D., ACTING HEAD ✓

By J. R. Boland
J. Robert Boland, Chemist

Beverly R. Sullivan
Beverly R. Sullivan, Chemist

JRB:kk
Att.

~~CONFIDENTIAL~~

REGRADED (Unclass) BY AUTHORITY OF J. J. Keech
BY Ch. Sec. Intel. Oper. Com. (NAME, GRADE & ORGANIZATION) 7 Jul 59 (OFFICER AUTHORIZED TO CHANGE)
DATE

~~CONFIDENTIAL~~

100 WEST WALNUT STREET
PASADENA, CALIFORNIA 91124
(818) 440-2000
Telex WH: 675-336

PROJECT DESCRIPTION

DISPOSAL OF CHEMICAL WASTES,
PROJECT DESCRIPTIONS

July 10, 1984

Rocky Mountain Arsenal Information Center
RIC Building 741
Attention: S. Michaels
SMCRM - TOE
c/o Rocky Mountain Arsenal
Commerce City, Colorado 80022

Dear Sherry:

Here are project descriptions for the chemical waste disposal study Parsons did for the Corps of Engineers at Rocky Mountain Arsenal.

Basically, they say the same thing, but since they were the only information I could find on this job, decided to send you copies of all three.

Sorry we weren't able to locate more material for you, but do hope you can use this information. Please let us know if we can assist you with anything else.

Cordially,



Kathleen A. Richter
Corporate Relations

KR:tm
Enclosures

FILE COPY

Rocky Mountain Arsenal
Information Center
Commerce City, Colorado



CHEMICAL WASTE DISPOSAL STUDY

LOCATION: Rocky Mountain Arsenal, Colorado

CLIENT: Corps of Engineers, Omaha District

OBJECTIVE: To study the disposal of chemical by-products and wastes from the various operations at Rocky Mountain Arsenal, and to recommend the most practical method of disposal.

Work Performed

Studies existing plant operations and disposal methods. Prepared economic evaluation of various processes to purify by-products and convert to salable materials. Conducted market survey for by-products. Recommended changes in plant operations and installations of by-product purification and recovery equipment valued at \$2,900,000. Sampled well waters for analysis, and consulted with agronomist and plant pathologist to develop program to determine if phytotoxic agents were being discharged from the chemical plants. Upon completion, the recommended changes and additions actually saved the Chemical Corps \$20,000 each day of full-plant operation by recovering valuable materials being wasted and from savings in disposal costs.

Description of Recommended Processes

Chemical Corps Plant No. 1

Valuable products were being lost in the anhydrous hydrogen chloride by-product gas stream, and our first recommendation was to install larger condenser and refrigeration capacity to reduce the loss of the valuable product.

A system was designed to absorb the impure acid gas in water, then purify the acid by fractional distillation. The pure hydrogen chloride is reabsorbed to form marketable 20° Baume acid. Conversion of pure hydrogen chloride to chlorine by various processes was investigated and discarded because of excessive costs.

Chemical Corps Plant No. 2

This plant produces a large tonnage of aluminum chloride hydrate and hydrogen chloride as by-products.

A system was designed to neutralize these by-products with caustic soda, separate the aluminum hydroxide floc, and recover solid sodium chloride as feed material to the existing chlorine plant.

STD.
9-27-63

AE4113



CHEMICAL WASTE DISPOSAL STUDY

CLIENT: Corps of Engineers, Omaha District
LOCATION: Rocky Mountain Arsenal, Colorado

* * * * *

Parsons undertook a detailed study to review existing plant operations and disposal methods for chemical by-products and waste materials at the Rocky Mountain Arsenal facilities. The study included an economic evaluation of various processes for purifying the by-products and converting these into salable materials; a market survey for by-products; sampling and analyses of well waters; consultations with agronomist and plant pathologist in developing a program to determine the amount of phytotoxic agents, if any, being discharged from the chemical plants. From the results of the study and analyses, recommendations were made as to the most practical method of disposal.

The study of Plant No. 1 revealed that valuable products were being lost in the anhydrous hydrogen chloride by-product gas stream. A plan was developed for installing a larger condenser and increasing refrigeration capacity to reduce these losses. A system was designed to absorb the impure acid gas in water, then purify the acid by fractional distillation. The pure hydrogen chloride is absorbed to form marketable 20° Baume acid.

Plant No. 2 was producing a large tonnage of aluminum chloride hydrate and hydrogen chloride by-products. A system was designed to neutralize these by-products with caustic soda, separate the aluminum hydroxide floc, and recover solid sodium chloride as feed material to the existing chlorine plant.

The recommended changes in plant operations and installations of by-product purification and recovery equipment was valued at \$2,900,000. Upon completion, the recommended changes and additions saved the Chemical Corps \$20,000 per day of full-plant operation by recovering valuable materials being wasted and by reducing disposal costs.

1113/668



X

CHEMICAL WASTE DISPOSAL STUDY

Project Location - Rocky Mountain Arsenal, Colorado

Client - Corps of Engineers, Omaha District

Work Performed - Performed studies and economic evaluations; conducted surveys and recommended changes.

Project Description - A detailed study was undertaken to review existing plant operations and disposal methods for chemical by-products and waste materials at the Rocky Mountain Arsenal Facilities. The study included an economic evaluation of various processes in purifying the by-products and converting these into salable materials; a market survey for by-products; sampling and analyses of well waters; consultations with agronomist and plant pathologist in developing a program to determine the amount of phytotoxic agents, if any, being discharged from the chemical plants. From the results of the study and analyses, recommendations were made as to the most practical method of disposal.

The study of Plant No. 1 revealed that valuable products were being lost in the anhydrous hydrogen chloride by-product gas stream. A plan was developed for installing a larger condenser and increasing refrigeration capacity to reduce these losses. A system was designed to absorb the impure acid gas in water, then purify the acid by fractional distillation. The pure hydrogen chloride is absorbed to form marketable 20° Baume acid.

Plant No. 2 was producing a large tonnage of aluminum chloride hydrate and hydrogen chloride by-products. A system was designed to neutralize these by-products with caustic soda, separate the aluminum hydroxide floc, and recover solid sodium chloride as feed material to the existing chlorine plant.

The recommended changes in plant operations and installations of by-product purification and recovery equipment was valued at \$2,900,000. Upon completion, the recommended changes and additions actually saved the Chemical Corps \$20,000 each day of full-plant operation by recovering valuable materials being wasted and from savings in disposal costs.